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The thermal and mechanical behavior of poly(ethylene terephthalate) fibers incorporating novel thermotropic liquid crystalline polymers/

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THE THERMAL AND MECHANICAL BEHAVIOR OF POLY(ETHYLENE TEREPHTHALATE) FIBERS INCORPORATING NOVEL THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

A Dissertation Presented

by

SCOTT LAWRENCE JOSLIN

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Polymer Science and Engineering

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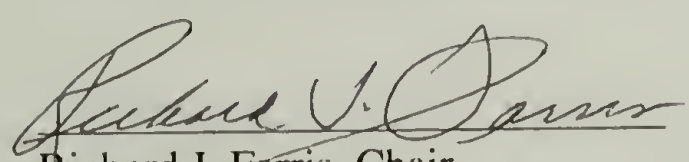
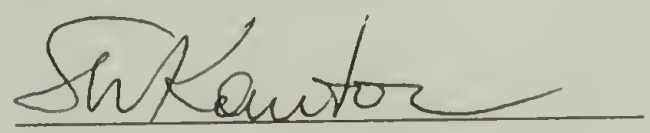


Richard J. Farris, Chair



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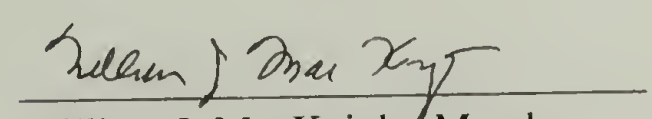

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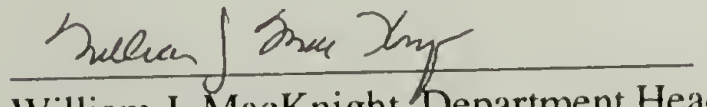

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My parents have been a constant source of support and absolute love. They are the foundation on which I'm built and more than anything else have made me who I am. They have also encouraged me to strive for my best and are always there when I need them. Words cannot express the feelings and appreciation I have for them.

Finally, I dedicate this project to my grandfather Earl Nelson. I will never forget his fascination with the future and its endless possibilities.

ABSTRACT

THE THERMAL AND MECHANICAL BEHAVIOR OF POLY(ETHYLENE TEREPHTHALATE) FIBERS INCORPORATING NOVEL THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

FEBRUARY 1994

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This dissertation explores the potential of improving the performance of poly(ethylene terephthalate) fibers by incorporating novel thermotropic liquid crystalline polymers. To determine if a system exhibited desirable characteristics, a screening procedure was developed to assess the various blends. Evaluations focused on blend compositions ranging from 2 to 20 wt. % LCP. Fibers were obtained by melt extrusion and the effect of processing conditions, i.e. spinning temperature, stretch ratio, and post treatment evaluated. The fibers were tested for mechanical performance, dimensional instability (shrinkage), and the development of shrinkage stresses. Test results were used to determine the critical parameters necessary for in-situ reinforcement and to develop strategies for improving LCP architecture and processing techniques.

The novel TLCP's incorporated into the PET were mesogenic copolymers containing either alternating or random flexible groups within the polymer backbone. The flexible moieties were used to promote compatibility between the PET matrix

phase and the TLCPs. Two systems were found to significantly improve fiber stiffness compared to neat PET fibers.

A Random Copolymer based on the reaction of oxyethylene substituted hydroquinone, ethylene glycol, and terephthaloyl chloride was found to effectively enhance the performance of PET fibers. Fibers containing only 5 % TLCP exhibited a 50 % increase in modulus, while maintaining an ultimate strength equivalent to the PET control. The thermal behavior of the 5 % blend, as determined by free shrinkage and force-temperature experiments, was similar to the PET control.

A segmented block copolymer consisting of rigid-rod, diad, and flexible coil segments was also found the improve the performance of PET fibers. At a concentration of 20 wt. percent, the alternating block copolymer, Triad2 (2:6:7), increased the tensile modulus of the fibers 40 % and decreased free shrinkage by 20 % compared to neat PET.

The mechanism of reinforcement for these systems is unclear, but morphological, thermal and mechanical evidence suggest that the TLCPs are modifying the PET matrix and not providing true mechanical reinforcement.

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CHAPTER 1

INTRODUCTION

1. 1 Background

Engineers are constantly being required to satisfy more stringent design criteria ensuring that demand will continue to grow for materials with higher tensile strength, modulus, thermal conductivity, heat distortion temperature, and lower thermal expansion. Polymeric composites are increasingly becoming the materials of choice to meet these needs. These materials are unique in that they provide engineers the opportunity to adjust material properties, by controlling constituents and microstructure, to meet desired stiffness and strength requirements. Polymer composites cover many classes of materials including particulate filled polymers, fiber filled materials, foams, and polyblends. Of particular interest in this work are liquid crystal in-situ composites.

Liquid crystalline in-situ composites are formed by the inclusion of a rigid rod polymer in an isotropic matrix. These systems may provide good mechanical performance while preventing technical difficulties associated with the presence of a filler which is solid in the processing stage(s). Solid fillers such as short glass fibers can cause significant wear on processing equipment, increase the molten polymer viscosity, and pose difficulties in compounding. For these and other reasons it would be highly desirable to develop in-situ composites since the reinforcing component is not actually present during processing of the resin, but develops upon solidification into highly oriented and high modulus inclusions.

Commercial liquid crystalline polymers (LCP's) are of interest as a reinforcement material for engineering thermoplastics due to their ability to be processed into highly oriented, anisotropic morphologies with high strength and stiffness. In addition LCP's offer a range of interesting properties such as low viscosity, low axial thermal expansion, and chemical resistance. Thus it is hoped that in-situ composites represent a feasible method for exploiting the desirable features of LCP's, but at a reduced cost.

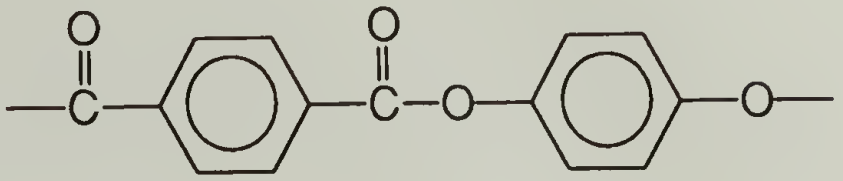
Several lyotropic systems have been investigated. Blends of poly(p-phenylene terephthalamide) PPTA with Nylon [1], PVC [2], and ABS [3] and blends of PBZT with poly(2,5,6-benzimidazole) (ABPBI[3,4]), poly(etheretherketone) (PEEK [7]), and Nylon [5-8] have been studied. However, thermotropic LCP's are currently the preferred reinforcement material for designing in-situ composites. The large scale interest in thermotropic systems is due to their ability to be used with conventional melt processing techniques and equipment without expensive and potentially hazardous solvents. Melt processing also permits a greater polymer through-put per unit time which reduces manufacturing costs.

1. 2 Thermotropic Liquid Crystalline Polymers

To achieve the desired structure and properties of Thermotropic Liquid Crystalline Polymer (TLCP) materials, it is necessary to take into account: molecular structure, phase behavior, rheology, processing and morphology.

1. 2. 1 Molecular Structure

Synthesis of thermotropic LCP's requires careful tailoring of the molecular architecture. The basic structure in liquid crystalline polyesters, shown in figure 1.1, are benzene rings linked at para positions through ester groups:



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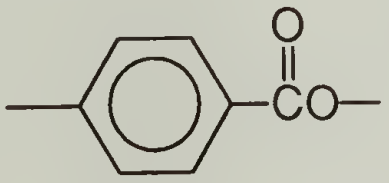

b

Figure 1.1. a) terephthalic acid plus hydroquinone and b) p-hydroxy benzoic acid (PHBA)

Several all aromatic polyesters have been synthesized and patented using these structures [9-11]. The homopolyester of PHBA synthesized by Economy and coworkers (11) was sufficiently stable to be compression molded at 440°C/28 MPa. The polyester doesn't melt until 610°C, but it will flow under the influence of heat and pressure due to a crystal - crystal transition at 350°C. Advantages of this material include excellent room and high temperature mechanical properties; the polymer retains approximately 60% of the room temperature flexural modulus at 300°C. However, the polymer cannot be processed using conventional processing techniques and equipment. The considerably high melting points and low decomposition temperatures of all aromatic polyesters prevent these materials from being melt spun or injection molded without thermal decomposition. In order to induce the

mesomorphic transition to occur below the decomposition temperature, it is necessary to introduce a limited amount of disorder into the polymer chain. Chain disorder introduces defects in the crystal lattice which may lower the crystalline melting point.

Copolymerization with controlled amounts of flexible or bent rigid moieties has been successful at improving polymer tractability [12]. See figure 1.2. Several thermotropic LCP's with sufficient processing windows have now been synthesized and characterized. Among the best known of these structures are copolymers of PHBA with 2,6-naphthalene diacetate and terephthalic acid (NDT/PHB), with ethylene terephthalate (PET/PHB), and with 2,6-hydroxynapthoic acid (HNA/PHB). Some commercially available copolyester LCP's are listed in Figure 1.3 [13].

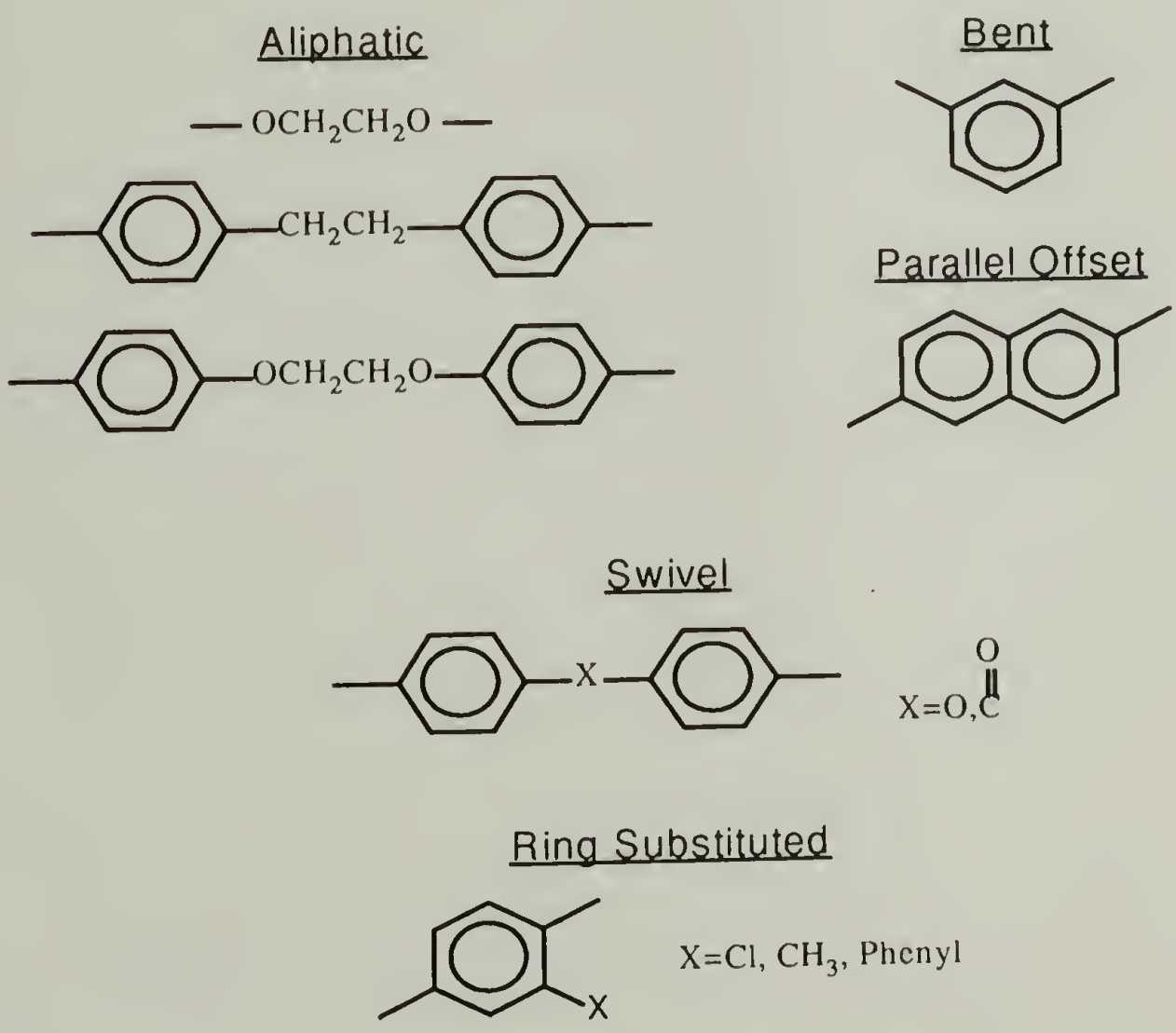

Figure 1.2. Flexible and bent rigid moieties used for improving the tractability of thermotropic liquid crystalline polymers.

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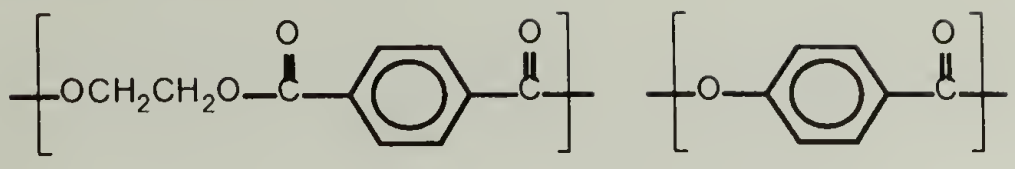

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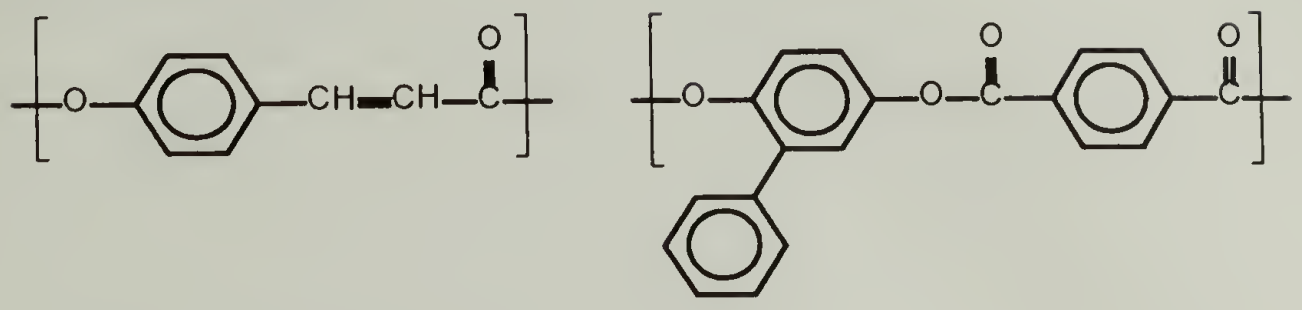
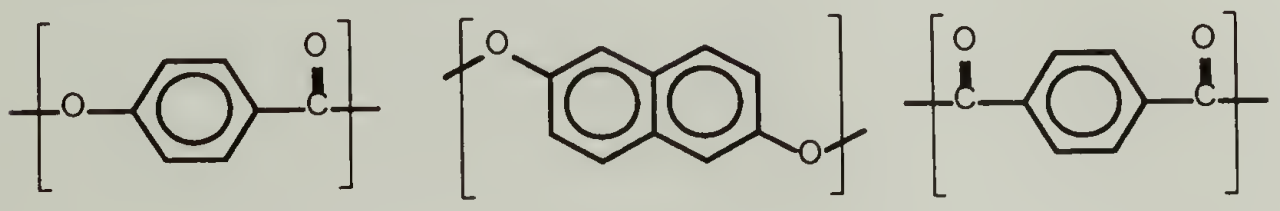


Hoechst Celanese (Vectra)



Amoco (Xydar)

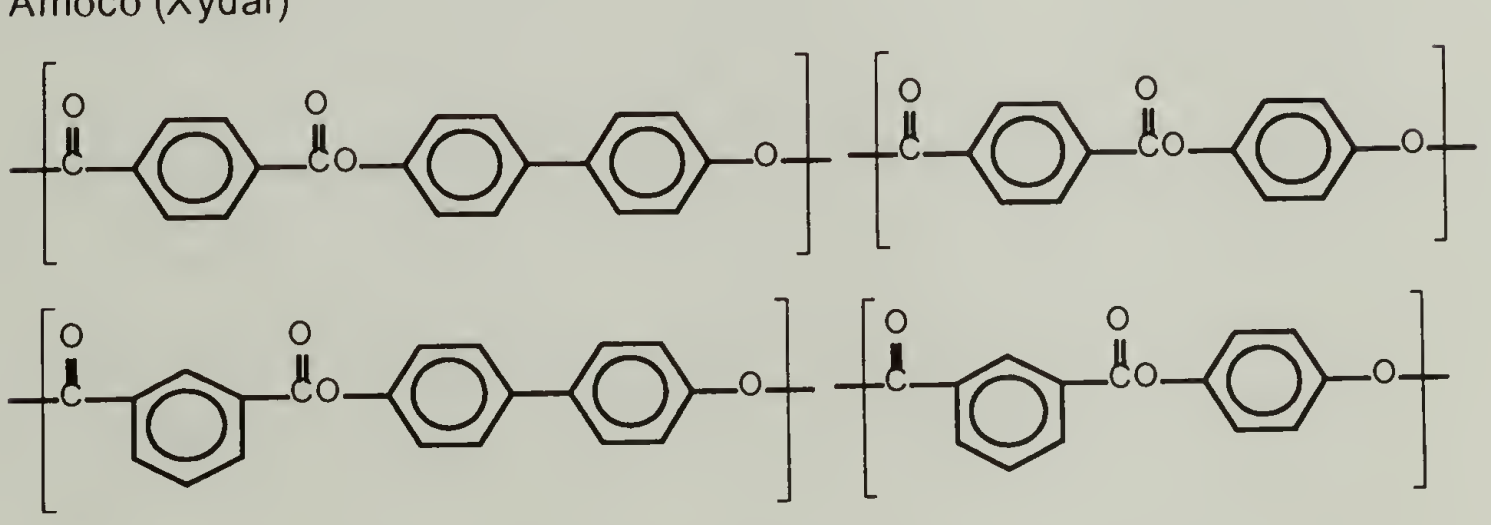


Figure 1. 3. Four commercially available aromatic LCP co-polyesters.

1. 2. 2 Phase Behavior

Three distinct organizational mesophases have been classified for liquid crystals: the nematic, smectic, and cholesteric. Structural differences between these phases are related to packing aspects and translational organization of the molecules. However,

all of the liquid crystal phases are distinguished by a unique director in the fluid. The director is a preferred orientation established by the parallelism of the average mesogenic unit. If orientation along a director is the only kind of long range order present in the material, it is classified as having a nematic phase i.e. there is no translational order in this phase.

The cholesteric phase is similar to a nematic in organization, with the additional feature of a cumulative twist in the director. The twist is due to the presence of a chiral center in the mesogen which causes an asymmetry of intermolecular forces between nematic layers. The twisting of the local nematic director results in an inherently biaxial or helicoidal structure.

The smectic phase, in addition to having a director, is also characterized by having at least one or more additional elements of long-range order. There are a number of smectic phases. For instance, in a smectic A phase the molecular centers lie on equidistant planes perpendicular to the director, while in a smectic B phase such planes are also present but there is an additional two-dimensional hexagonal lattice within each plane. It is important to note that the increased translational organization in the smectic phase(s) lowers chain mobility relative to a nematic phase and causes a tendency for defects, i.e., chain ends or flexible moieties, to segregate between layers. Thus only the nematic state offers the highly oriented, non chain end registered structure in the solid state desirable for high modulus and strength applications.

1. 2. 3 Rheology

Knowledge of the rheological behavior associated with liquid crystallinity is essential for the processing of these polymers into high performance structures. However, rheological characterization of the liquid crystalline state is difficult since it

is very different from and more complicated than the isotropic state. Investigations into the rheological behavior of TLCP's are numerous in the literature. The velocity fields of simple shear flow, small strain dynamic oscillation, and uniaxial extension have been studied with shear flow receiving the majority of attention [12-31].

In general compared to isotropic polymers of similar molecular mass and distribution, TLCP's have low viscosities [25,26,30,31], long relaxation times, [23,27,31,33] are easily oriented, [12-14,17,18,26,29,30,31] and exhibit little or no die swell [24,26,28]. Since all of these properties provide advantages during processing, it is desirable to understand their origin. Studies on the shear viscosity function of aromatic polyesters suggest that the rheological behavior of liquid crystals is strongly dependent upon the orientation of the molecules with respect to a given flow field. It has been proposed [29,32] that all LCP's posses an orientation dependence on viscosity of a characteristic shape, having three distinct regions: i) a shear thinning at very low shear rates, ii) a plateau region of nearly constant viscosity, and iii) another shear thinning region at high shear rates. These regions correspond to transitions in the texture of the nematic phase. The quiescent nematic phase can be pictured as an aggregate of domains separated by defects, each characterized by a preferred chain orientation indicated by the director [23]. The overall molecular orientation, as determined by both the alignment within the domains and their distribution, can be isotropic. At low deformation rates, region I, these domains begin to deform. With increasing deformation a constant viscosity plateau appears, region II, where no net orientation or decrease in defect concentration is observed. At higher deformation rates the dispersed polydomain structure is gradually transformed into the monodomain phase associated with region III. In short, when the defect rich structure of a quiescent nematic phase is subjected to a flow field, the defect structure is affected and the corresponding domain texture (size and orientation) changes. Ideally

the system may be converted into a monodomain, in which all defects are absent and the molecules are uniformly oriented.

1. 2. 4 Processing and Morphology

Several investigators [12-14,17,18,26,30] have observed that polymeric nematic liquid crystals easily orient in elongational and high shear flow fields. These flow fields are present in injection molding, extrusion, and spinning processes. Thus investigators are focusing on these particular manufacturing methods in an effort to exploit the high potential of TLCP's. Several TLCP injection molding compounds are now available. See Table 1.1. All of these compounds have tensile and flexural moduli in the range of 7 to 21 GPa and exhibit low viscosities and low linear coefficients of thermal expansion. Although the moduli are comparable to those of glass-filled semicrystalline polymers, the low viscosity and thermal expansion of the nematic LCP's is unique. Low viscosities permit heavy TLCP loadings and injection molding of long thin mold sections, while the low thermal expansion allows the manufacture of dimensionally stable and high precision parts.

Table 1.1. Physical properties of some TLCP's following injection molding.

	Victrex (SRP-1)	Victrex (SRP-2)	Vectra (A-900)	Xydar (SRT-300)	Ekonol (6000)
Density (g/cc)	1.38	1.38	1.4	1.35	1.4
Melting Point (°C)	----	----	280	420	321
Tensile Modulus (GPa)	----	----	10	14	8
Tensile Strength (MPa)	230	220	170	110	----
Coefficient of Thermal Expansion (ppm/°C)	6	6	6	0	6

The microstructure of injection molded TLCP's subjected to complex flow fields are composed of hierarchial fibril units [12,15,16,34]. The rigid rod molecules are arranged in fibrous interconnected microlayers, which are ordered in sublayers, which are arranged in a macroscopic layered structure most often referred to as a skin-core structure [34]. Orientation variations in the layers result in property anisotropy in the flow and cross flow directions. The number of layers and their orientation depends on sample geometry and processing conditions. In general, there is a highly ordered top layer, the skin, and a less oriented core layer while the layers in between have various degrees of orientation. The highly oriented structure and superior mechanical properties of the skin results from quenching of the LCP at the cold wall of the mold. The material at the center may relax producing less oriented LCP that does not exhibit high mechanical performance.

Extrusion is an effective method for forming TLCP rods, but film and sheet geometries are difficult. During the extrusion process the linear chains, close-packed in the fluid nematic domains, orient easily in the convergent flow field of the die. However, the high orientation in the flow direction causes unbalanced properties in the machine and transverse directions. This combined with the characteristically low elongation of LCP's makes it difficult to draw biaxial films or sheets sufficiently for useful, balanced properties. Some mechanical properties of extruded films and sheets have been reported. Films and sheets made from Vectra, a Hoechst Celanese product, have tensile strength and moduli of 35 to 500 MPa and 3 to 35 GPa, respectively [27].

Fiber spinning has proven to be the easiest and most effective method of obtaining oriented TLCP's. A typical fiber spinning process encompasses two distinct types of deformation: shear and elongational. The high orientation in LCP fibers results from elongational deformation found in the converging flow field of the

spinneret and the extensional flow field of the spin line [12,15-17,26,30]. For instance PET40/PHB60, a statistical copolyester containing 60 mol percent PHB, does not develop appreciable chain orientation prior to exiting the die, although the material experiences a large amount of shear deformation in the capillary [15]. In contrast, the orientation development in the elongational flow field associated with melt stretching is extremely efficient. Jaffe and coworkers [12] have shown that the diffraction pattern of a fiber with a stretch ratio of 3 is almost identical to that of a fully stretched fiber.

Melt stretching also results in the rapid development of excellent mechanical properties. Investigations of fiber microstructure, to determine the origin of these properties, have been reported for many TLCP's [12,15-17,33,34,37]. Thermal analysis, wide angle X-ray diffraction, optical and electron microscopy are the most common techniques for investigating the morphology of as-spun fibers. The molecular organization of oriented TLCP's is that of a nematic glass exhibiting orientation and order parallel to the fiber axis. Scanning electron microscopy performed on fiber cross sections have shown highly fibrillar structures that have a distinct hierarchy similar to injection molded samples. The hierarchy in a 20 μm PET40/PHB60 LCP fiber consists of 5 μm macrofibrils, 500 nm fibrils, and 50 nm microfibrils [12].

Tensile moduli of wholly aromatic, thermotropic copolyester fibers are typically in the range of 400 to 1100 g/d (50-150 GPa) depending on the specific chemical composition. Fibers from polymers containing aliphatic or m-phenylene moieties show lower modulus values and are in the range of 400 to 700 g/d (50-85 GPa). In contrast to aramid fibers, these moduli do not improve significantly with heat treatment.

The tenacity of as-spun wholly aromatic fibers is typically in the range of 5-14 g/d (0.5-2 GPa) and is primarily a function of polymer molecular weight. In general, polymers containing flexible or m-phenylene moieties show slightly lower tenacity

levels. The tenacity of heat treated fibers are in the range of 20-40 g/d (2.5-5 GPa) and no systematic variation with polymer composition is observed. Tenacity increases with heat treatment are due to increased molecular weight (solid state polymerization) and not to structural perfecting processes [38].

Melt spinning of highly oriented fibers is currently the only method of obtaining the mechanical property potential of thermotropic LCP's. Several companies are developing high performance TLCP fibers for commercial use in composite applications. As illustrated in Table 1.2, the high mechanical properties and tractability of TLCP fibers have made them attractive candidates as reinforcing fibers. However, it remains to be seen if the processing advantages are sufficient to displace the now well established aramid fibers and the high performance polyethylene fibers. Use of TLCP's as a processing aid or as an in-situ reinforcement agent for conventional polymers may be a more realistic application for these polymers.

Table 1.2. Physical properties of high performance reinforcing yarns.

	Kevlar 29	Kevlar 49	Kevlar 149	Vectran A950	Ekonao 1	Carbon/Graphite Hi Str.	Carbon/Graphite Hi Mod	Glass S-2
Density (g/cc)	1.44	1.44	1.47	1.4	1.4	1.77	1.96	2.49
Melting Point (C)				327-331				
Tensile Strength (MPa)	2930	2930	2345	2472-3090	3708	3595	1904	3518
Tensile Modulus (GPa)	67	114	141	84-104	140	234	519	88
Elongation (%)	3.6	2.5	1.45	2.2-2.5	2.4	1.5	0.4	4.0

1. 3 TLCP Blends with Isotropic Polymers

Using TLCP's as one of the components in polymeric blends may lead to very interesting systems. The combination of TLCP's with conventional random coil polymers may allow material properties or processing parameters to be cost effectively

tailored to specific needs and applications. Most of the work to date has centered on melt-blending thermotropic copolyesters, such as Vectra or Xydar, with engineering thermoplastics (PET, PBT, PC, PEEK, and nylons). These investigations may be separated into three main categories: i) phase behavior and thermal studies, ii) rheology and processing, and iii) mechanical properties and morphology.

1. 3. 1 Phase Behavior

Various investigators have reported that the rate and degree of crystallization of flexible-coil polymers increased with the addition of LCP's [39-44]. Joseph and coworkers [42] have shown an increase in the rate of PET crystallization with the addition of increasing amounts of the liquid crystalline polyester PET40/PHB60. In addition to the improved crystallization rate, an overall increase in the degree of crystallinity is observed. Misra et al. [43] also studied blends of poly(ethylene terephthalate) using several different TLCP's and found that the crystallization rates for the blends were higher than that of pure PET. They suggested that the surface of the rigid LCP acted as a nucleating agent for the crystallization of the matrix polymer. Although these studies did not report an upper limit to the nucleation effect, Jo et al. [44] observed a maximum nucleation rate at concentrations as low as 5 to 15 weight percent LCP in blends with poly(butylene terephthalate). They suggested that increasing LCP domain sizes at higher concentrations caused the nucleation of poly(butylene terephthalate) to become less efficient.

The miscibility behavior of blends containing a TLCP and a random coil polymer have been widely investigated using DSC, X-ray diffraction, optical and scanning electron microscopy [45-51]. Several studies have focused on the behavior of PET/PHB copolyesters [45,47,48]. PET/PHB copolyesters are statistical copolymers

that exhibit two phases: a PHB rich phase and a PET rich phase [37]. Phase behavior studies of PET/PHB with PBT as matrix have shown that the PET-rich phase of the copolyester was miscible with PBT whereas the PHB-rich phase was not [45]. When PC was used instead of PBT, it also was partially miscible with the PET-rich phase of the LCP [47]. In general, however, thermotropic polyesters melt blended with isotropic polymers exhibit no miscibility and tend to be incompatible. Blends of polystyrene with PET/PHB copolyesters containing 30,60, and 80 percent PHB were found to be completely immiscible [51].

Nobile and coworkers [50] reported complete miscibility of PC with PET40/PHB60 after annealing the LCP/PC melt. Annealing at elevated temperatures allowed transesterification to occur resulting in a miscible system. Similar annealing studies with PET blends did not lead to a miscible system, but the melting temperature of the PET was reduced by 42°C [52]. Single phase behavior was observed in blends of PET and a tercopolymer of PHB, bisphenol A, and terephthalic acid (TA) after transesterification [52]. These studies suggest that transesterification reactions increase the compatibility of liquid crystalline copolyesters with isotropic polyesters.

1. 3. 2 Rheology and Processing

A major advantage of blending LCP's with thermoplastic polymers is that the LCP may act as a processing aid. Thermotropic polymers exhibit low viscosity and near zero extrudate swell thus blends are actually easier to process than the neat random coil polymer. To take advantage of these unique TLCP processing characteristics the temperature range of the anisotropic LCP phase must overlap with

the melt processing temperature of the conventional polymer. The anisotropic nematic phase reduces the viscosity of the thermoplastic allowing processing temperatures to be decreased. Lower processing temperatures reduce energy consumption and degradation reactions while lower viscosities facilitate the filling of large or complex geometries.

Processing aids typically constitute 20 percent or less of the total system. There have been several rheological investigations using PET/PHB type copolyesters as potential processing aids. Blizard and Baird [53] studied blends of PC and nylon 66 with PET40/PHB60 and observed a significant viscosity reduction at high shear rates. Similar results were reported by Zuang [51] and Lee [55] for this LCP blended with PC, PVC, and PET using injection molded samples. The high shear rates used in Blizard and Baird's investigation were obtained using a capillary rheometer where the simple shear in the capillary is preceded by an extensional or convergent flow in the die entrance region. Although the aspect ratio of the die is large to minimize entrance effects, it remains unclear which flow field, simple shear or elongational, is responsible for the observed reduction in viscosity. Similar ambiguities are associated with injection molding.

HNA/PHB is another liquid crystalline copolyester that has been widely studied as a potential processing aid for engineering thermoplastics. For instance, blending an amorphous polyamide under high shear conditions with as little as 5 percent HNA/PHB resulted in a large reduction in viscosity compared to the neat material [56]. Similar results have been reported for blends of HNA/PHB with poly(acrylate) [57] and poly(ether sulfone) (PES) [58]. The PES blend exhibited a four fold decrease in viscosity at high shear rates with the addition of only 2 percent LCP.

The reduction in viscosity with LCP addition is not necessarily an additive process. Chung and coworkers [59] investigating HNA/PHB blended with nylon 12

found a minimum in viscosity at a concentration of 10 weight percent LCP and a maximum at 20 percent LCP. This complex behavior was attributed to changes in the morphology of the system. Below 10 percent the LCP domains were well dispersed in the nylon 12 and the system exhibited interfacial slip, thereby reducing the resistance to flow. At 20 weight percent LCP, two continuous phases developed resulting in a sharp increase in viscosity. It must be noted that this investigation was carried out at relatively low shear rates which is inefficient at orienting LCP's.

Studies of PC blended with 5% HNA/PHB/TA/HQ have shown a 68 percent drop in viscosity at high shear rates. The continuous phase dominated the rheological behavior of the blend and determined the shape of the viscosity vs. shear rate curve [60]. Blends with a continuous PC phase exhibited a curve similar to neat PC with the exception that as the LCP content increased shear thinning occurred at lower shear rates. A continuous LCP phase was observed at 40 to 50 percent loading levels and the corresponding flow curves were similar to neat LCP.

1. 3. 3 Mechanical Properties and Morphology

Mechanical properties and morphologies of flexible coil/LCP blends have been reported in a number of studies [43,49,50,53,55,56,58-81]. The primary purpose of the LCP in these studies was to provide mechanical reinforcement for isotropic thermoplastic polymers. Thermotropic polymers can form fibrous domains or inclusions in a matrix polymer when melt blended. Due to the potential strength and stiffness of thermotropic polymers, these fibrous inclusions may act as a reinforcement agent, much like chopped glass.

Scanning electron microscopy and X-ray diffraction were the most widely used techniques for elucidating the geometry and orientation of the LCP phases within the

thermoplastic. The size, shape, and distribution of the LCP phase influenced the mechanical properties of the blends. Variables such as the composition, processing conditions, and relative viscosity of the blends have been investigated.

The relative viscosity is simply a ratio of the inclusion viscosity to the matrix viscosity.

$$\lambda = \frac{\eta_i}{\eta_m}$$

Fiber studies on 20 percent PET40/PHB60 blended with PC have shown the importance of a having relative viscosity less than or equal to one for LCP fibril formation [54,56]. Blends extruded and drawn at 260°C contained spherical LCP domains while blends extruded at 210°C had fibrillar domains oriented in the flow direction. The blends processed at 210°C had a relative viscosity of approximately one which is favorable for deformation of the dispersed phase, however, for relative viscosities much greater than one the dispersed phase does not deform or orient in the flow field and may be considered rigid.

Blends using HNA/PHB [60-62] based LCP's as a reinforcement agent for PC rods have resulted in greatly improved mechanical properties compared to neat PC. Blizard, et al., [60] observed an order of magnitude increase in tensile modulus as the stretch ratio was incremented from 1 to 1000. The large amount of extensional deformation imposed on the rods by stretching promoted fibril formation and chain orientation in the flow direction. Fibril formation is important since spherical inclusions have only a small influence on tensile properties, whereas blends with a fibrillar morphology generally experience an increase in mechanical performance.

Ramanathan and coworkers [80] investigated PET40/PHB60 blended with poly(phenylene sulfide) and found that the blend microstructure was dependent on composition and not on stretch ratio. Ko and Wilkes [81] also reported that PET blended with HNA/PHB did not exhibit increased mechanical performance until 80

weight percent LCP. It was suggested that a critical LCP domain size was required for fibril formation of the LCP phase. This behavior seems to be atypical and it is generally reported that mechanical properties, strength and stiffness, increase monotonically with increasing LCP content, while elongation to break is decreased. Correspondingly, as the LCP content increases the mode of failure changes from ductile to brittle.

Observations of a skin core morphology are prevalent throughout the literature, particularly in samples that have been injection molded or extruded [53,54,60,61,71,76,77]. Silverstein and Baer [76,77] investigated the microstructure of injection molded samples of HNA/PHB blended with PET. The system had five different layers distinguishable through changes in the size, shape, and orientation of the LCP domains. The top layer is highly oriented in the injection direction and contains rodlike LCP domains 1-2 mm in diameter. Fibril formation and orientation progressively decreased in the remaining layers. No discernible orientation or fibril formation was observed at the sample center. With increasing LCP content the orientation of the layers increased but the general trend of decreasing orientation towards the core was still followed. Similar observations have been made with other matrix polymers i.e. nylon 66, PC, and PBT [53,54,60,61,71].

Finally an added benefit of in-situ composites may be an increase in dimensional stability. Nicolais and coworkers [50] reported increased dimensional stability of drawn polystyrene by adding five weight percent of LCP. The authors suggested that the elongated and oriented LCP domains restrained the matrix from thermal dimensional change.

1. 4 Dissertation Overview

Several novel blend systems containing semi-rigid thermotropic liquid crystalline polymers and poly(ethylene terephthalate) have been investigated. The work focuses primarily on the ability of the TLCP's to improve the performance of PET fibers. To determine if a system exhibits desirable characteristics, a screening procedure has been developed to assess the various blends quickly and efficiently. Limited amounts of liquid crystalline polymer, typically 6 to 9 grams, require evaluations to focus on compositions ranging from 2 to 20 wt.- % LCP. Fibers are obtained by melt extrusion and the effect of processing conditions, i.e. spinning temperature, stretch ratio, and draw ratio are evaluated. Residence times in the extruder are kept to a minimum to prevent transesterification and degradation. The fibers are tested for mechanical performance, dimensional instability (shrinkage), and the development of shrinkage stresses. Test results are used to determine the critical parameters necessary for in-situ reinforcement and to develop strategies for improving LCP architecture and processing techniques.

The thermotropic LCP's investigated in chapter two were specifically designed to determine the type of block copolymer that yields maximum PET reinforcement. Two alternating block copolymers and a random copolymer were evaluated. These systems have poly(ethoxy 1,4-phenylene terephthalate) (PME) mesogenic units with either poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET) flexible moieties incorporated into the main chain. A copolymer composed of poly(1,4-phenylene terephthalate) with butoxyethoxy flexible side chains was also investigated. The influence of composition, temperature and draw ratio on the LCP phase morphology and the resulting blend properties have been examined. Simple composite theory was used to analyze the dependence of tensile modulus on blend

composition. Differential scanning calorimetry was also performed to determine if the LCP phase had any influence on the crystallization behavior of PET.

The thermotropic LCP's investigated in chapter three were specifically designed to determine the optimum molecular structure necessary to attain good compatibility and maximum reinforcement of PET fibers. Six different alternating block copolymers were screened. Variables that were examined included wt. % mesogen content, flexible block size, and mesogenic block size. The influence of LCP composition, spinning temperature, and draw ratio on blend performance has been determined.

In the previous chapter the possibility of improving upon the properties of neat PET fibers by incorporating novel TLCP block copolymers was investigated. One particular block copolymer system exhibited a 40 % increase in fiber modulus without causing matrix embrittlement. The objective of chapter four was to determine whether the LCP modified the PET matrix phase or provided true mechanical reinforcement of the fiber. Since the block copolymer was specifically engineered to be compatible with PET, a model system using a polycarbonate matrix was designed to elucidate the mechanism of property enhancement. Fiber compositions containing 20 wt. percent TLCP are compared. The effect of post treatment on the LCP phase and the mechanical and thermal performance of the blends is observed.

The results of this work are reviewed and the main conclusions are summarized in chapter five. Based upon the results of this investigation, recommendations for future research on a new generation of LCP's with improved architectures are discussed. Experimental methods for determining the mechanism of fiber reinforcement are also suggested.

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CHAPTER 2

TLCP'S WITH FLEXIBLE MOIETIES BLENDED WITH POLY(ETHYLENE TEREPHTHALATE)

2.1 Introduction

Poly(ethylene terephthalate) (PET) fibers are used in a variety of applications including: textiles, tire cord, and composites. Depending upon the final application, the properties of the fiber can be tailored by adjusting processing parameters such as molecular weight, spinning speed , draw ratio, and drawing temperature. However the demand for higher performance PET is continually increasing due to more stringent product requirements. Recently, the production of PET fiber with greater moduli, strength, and dimensionally stability has been the subject of intense research [1-5]. These studies have focused on structurally modifying PET fibers by mechanical and/or thermal treatments. Another approach which has not received much attention, would be to blend PET with a high performance thermotropic liquid crystalline polymer (TLCP).

TLCP's offer a range of potential benefits such as high strength and stiffness, low viscosity, and low thermal expansion. Several investigators have been able to improve the stiffness and dimensional stability of extruded and injection molded articles simply by incorporating low concentrations of a TLCP material. These performance enhancements have been attributed to in-situ reinforcement of the engineering thermoplastic matrices by an oriented TLCP phase [6-10]. The moduli of the extruded and injection molded systems, containing 10 to 20 wt. percent TLCP, were typically reported to be in the range

of 5 to 12 GPa. This stiffness increase is considerable since the modulus of amorphous PET is only about of 2 GPa. However these modulus values are not sufficient to improve upon the mechanical performance of neat PET fibers. The tensile modulus of high molecular weight PET fibers can attain values in the range of 14 to 17 GPa just by carrying out cold and/or hot drawing post-treatments. Therefore in order to successfully apply the concept of in-situ reinforcement to PET fiber spinning, the TLCP material must demonstrate the ability to reinforce a high performance matrix material. If successful, PET fibers blended with a TLCP could have greater mechanical performance and thermal stability than currently obtainable with neat PET. Furthermore due to their low melt viscosity TLCP's may function as a processing aid [11-13] permitting higher molecular weight PET to be processed.

Another potential disadvantage associated with blending commercial TLCP's with engineering thermoplastics is that the majority of the thermoplastics investigated were found to be incompatible with TLCP reinforcing agents. This incompatibility has resulted in matrix embrittlement, skin-core morphologies, and poor interfacial adhesion between the blend components at low to moderate TLCP loading levels [14-16]. PET embrittlement by the addition of a TLCP would be catastrophic since PET fibers must undergo significant drawing to attain maximum performance. Thus in order for this approach to be successful the TLCP must improve the performance of PET fibers at low concentrations without embrittlement. This would allow post-treatment of the fibers and maximize cost effectiveness since the expensive TLCP would be used in small quantities.

The objective of this study was to determine if properties superior to neat PET fibers could be achieved by blending with novel liquid crystalline polyesters. The following TLCP architectures have been investigated: 1) mesogenic copolymers containing either alternating or random flexible units and 2) rigid rods with flexible side groups. The incorporation of flexible units into the TLCP's should promote compatibility

between the PET and the TLCP's. Compatibility for this study is defined as a post-treatable fiber with enhanced performance characteristics. Miscibility is not desired since a two phase morphology is regarded as necessary in order to obtain the processing and mechanical benefits associated with TLCP's.

Due to limited amount of the TLCP's, a screening procedure has been developed to determine if a blend system exhibits desirable characteristics. Compositions varying form 5 to 20 wt. % LCP are commercially interesting and therefore evaluations focused on this range. Fibers were prepared by melt extrusion followed by cold and hot drawing. Fiber performance was evaluated based on tensile properties, dimensional instability (shrinkage), and the development of shrinkage stresses.

2.2 Materials

The thermotropic LCP's used in this study are a group of novel polymers kindly synthesized by Drs. Lenz and Kantor's group at the University of Massachusetts, Amherst. The polymers have been specifically designed in an effort to enhance compatibility between the LCP's and poly(ethylene terephthalate) (PET). The following structural approaches have been investigated: 1) block copolymers consisting of rigid rod and flexible coil segments and 2) a copolymer composed of a rigid-rod backbone with flexible side groups.

Two alternating block copolymers have been investigated [17]. These systems have poly(ethoxy 1,4-phenylene terephthalate) (PME) mesogenic units with either poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET) flexible segments incorporated into the main chain. Figure 2.1 shows the rigid-rod and flexible segments used in these block copolymers. The oxyethylene substituents incorporated into the mesogenic unit should lead to polar interactions with the ester linkages of the matrix

polymer promoting compatibility. The PET or PBT flexible segments in the main chain should also enhance compatibility with the PET matrix.

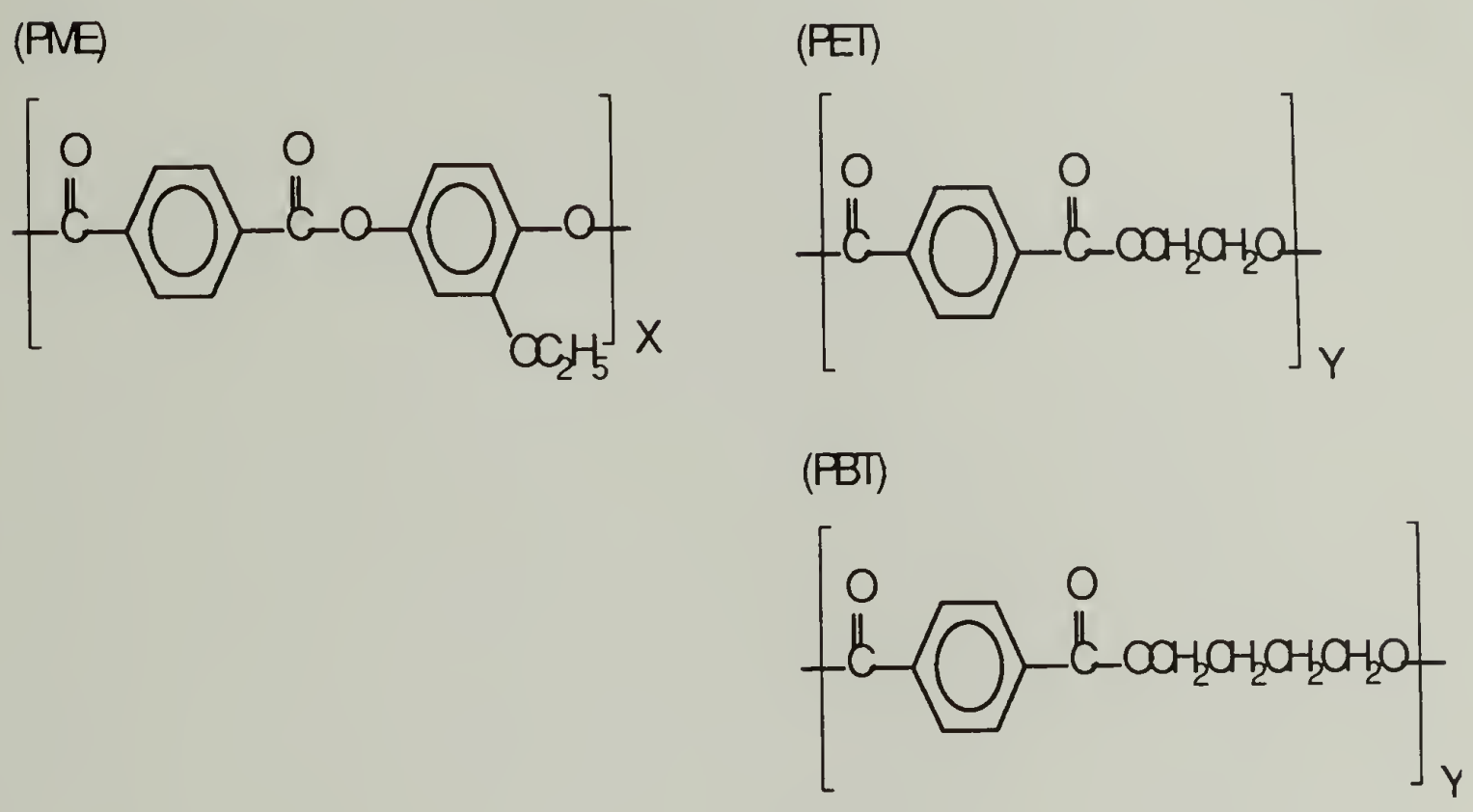


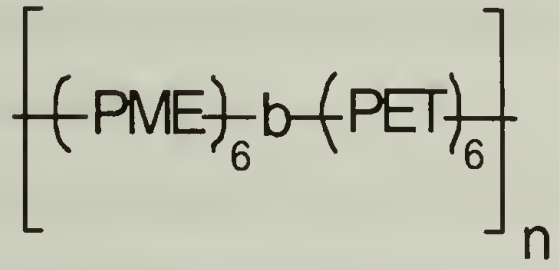
Figure 2.1. The rigid-rod and flexible segments incorporated into the alternating block copolymers.

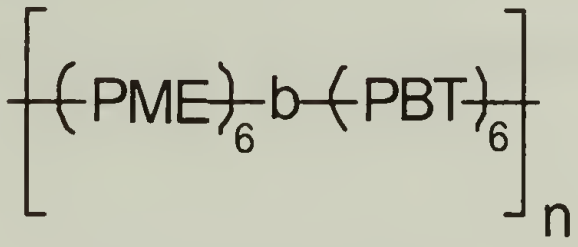
Although the flexible PBT units are not identical in architecture to the matrix polymer, PBT is miscible with PET [18]. Furthermore, the PBT blocks may also act as a nucleating agent for the PET matrix since PBT and PET do not co-crystallize [19]. Thus flexible PBT segments should be a suitable candidate for attaining compatibility with a PET matrix. Ultimately it's hoped that compatibility can be improved by incorporating a flexible block in the main chain whether it be PET or PBT. Figure 2.2 shows the polymer designations and structures selected to blend with PET for this investigation.

A random block copolymer has also been investigated. The copolymer was prepared by the reaction of oxyethylene substituted hydroquinone, ethylene glycol, and

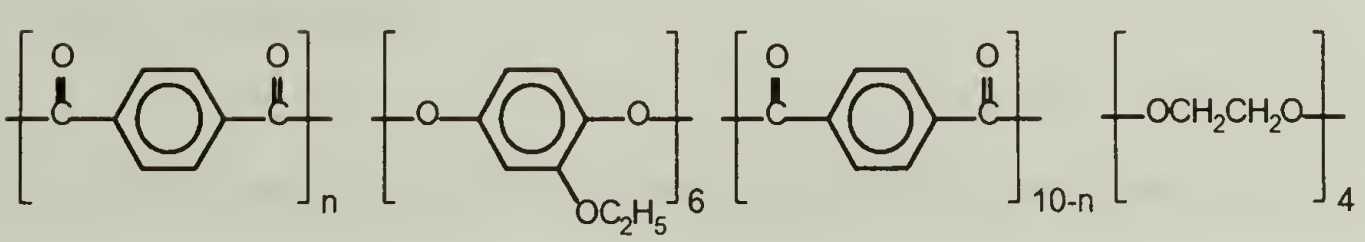
terephthaloyl chloride [20]. The copolymer incorporated a 60 to 40 ratio of oxyethylene substituted hydroquinone to ethylene glycol. This polymer has flexible side groups and PET moieties randomly distributed along the polymer backbone in an effort to achieve compatibility with the PET matrix.

Alternating Block Copolymers





Random Copolymer



PBEM Copolymer

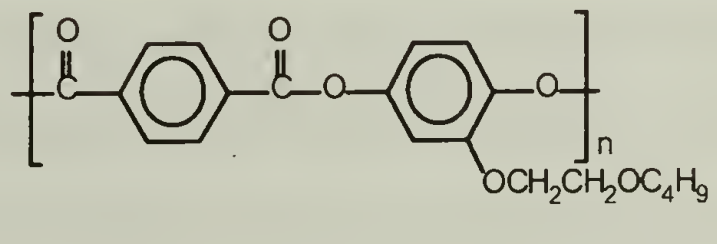


Figure 2.2. The copolymer designations and structures used for blending with PET.

The PBEM copolymer has a rigid backbone composed of poly(1,4-phenylene terephthalate) with butoxyethoxy flexible groups as side chains. As in the previous polymers the flexible side substituents should lead to polar interaction with the ester linkages of the PET matrix. The length of the side substituent was increased since flexible moieties were not incorporated into the main chain.

The amount of material available for blending and property determination was limited to approximately 7 grams for each polymer, thus the mechanical properties of the neat copolymers could not be determined.

The fiber grade PET used in this study was kindly provided by the Akzo Corp. The material had a reported melting transition of 273°C and an inherent viscosity of 2.04 (dL/g). The PET was blended as received without further purification.

2.3 Experimental

2.3.1 Thermal Characterization

The transition temperatures of the liquid crystalline block copolymers were measured calorimetrically using a TA Instruments 9900 differential scanning calorimeter. Temperature calibration was performed using an indium standard. Samples of approximately 10 mg were initially heated in a nitrogen atmosphere from 30 to 300°C at a heating rate of 20°C/min, followed by quenching with liquid nitrogen. Samples were then reheated to 300°C at a heating rate of 20°C/min. The reported transitions are the maximum peak temperatures observed during the second heating run.

The degradation temperatures in air were also measured using a TA Instruments 951 thermogravimetric analyzer. Samples were scanned from room temperature to 600°C at a

heating rate of 20°C/min. The reported degradation temperature corresponds to 0.5 % weight loss.

2.3.2 Fiber Formation

Powders of the thermotropic polyesters and PET were tumble mixed for 24 hrs. The amounts of block copolymer used in the blends were 5, 10, and 20 % by weight. The mixed polymer powders were then compression molded using a Carver laboratory press at 270°C for 1 minute. The compressed sample was consequently ground in an analytical mill to a particle size less than 1000 microns and vacuum dried at 120°C for a minimum of 24 hours. Compression molding followed by grinding was a convenient procedure for obtaining particles that effectively fed into the mini-extruder.

Once thoroughly dried the blends were extruded and spun into fibers. Extrusion was carried out with a ¼ inch Randcastle single screw mini-extruder. The mini-extruder has four temperature zones which may be varied independently. The feeding, compression and melting sections, zones one, two and three respectively, were set at 220°C, 260°C and 280°C. The temperature of the die zone was varied to observe the effects on fiber spinning. The ability to obtain a uniform melt without die swell was the main criteria for determining the die temperature. The screw speed was held constant at 30 rpm corresponding to a flow rate of 1.5 g/min. and a polymer residence time of two to four minutes within the extruder. The residence time in the extruder was kept to a minimum in order to reduce the possibility of transesterification reaction between the blend components.

Upon exiting the die of the extruder, the polymer was stretched using a custom built take-up device. A take-up speed of 75 m/min. was used for all systems which corresponds to approximate stretch ratios of 250 to 400. The stretch ratio for each system was

determined as the ratio between the die and the stretched extrudate cross-sections (A_0/A_f). The round hole capillary die had a diameter of 1575 μm and an aspect ratio of ten. Fiber diameters were determined by optical microscopy.

A two step post-treatment process was performed immediately following the spinning process. The heat treatment of poly(ethylene terephthalate) fibers is an important processing stage that determines the ultimate properties of the material. Post drawing was accomplished using a continuous process between optoelectronically monitored feed and take-up spools. Cold drawing was performed at 85°C using a standard laboratory hot plate. The speed of the feed spool was kept constant at 5 m/min while the speed of the take-up winder was continuously monitored and increased until a stable neck was observed. For neat PET this occurred at a draw ratio of 3.5.

Hot drawing was accomplished using a similar procedure at a temperature of 205°C. The maximum draw ratio was determined by slowly increasing the speed of the take-up spool until excessive filament breakage occurred. The speed of the take-up spool was then decreased until drawing could proceed for at least two minutes without filament breakage. For neat PET this corresponded to a maximum hot draw ratio of 1.5 and a total draw ratio (DR) of 5 for the fiber. The total draw ratio was calculated as the ratio between the as-spun and final post-treated fiber cross-sectional areas. All samples were collected and tested at the maximum draw ratio unless otherwise specified.

2.3.3 Tensile Testing

Tensile tests were performed on an Instron 1113 tensile tester connected to a personal computer. Specimens were affixed to paper tabs with an adhesive in order to facilitate mounting and alignment. Fiber diameters were measured using an Olympus microscope equipped with a calibrated scale accurate to ± 0.5 microns. A minimum of

five diameter measurements per fiber were obtained. The applied strain rate was 10 percent elongation per minute, with an initial gage length of 50 mm. A 550g Toyo TI550 load cell was used to measure the fiber load. The Young's modulus was determined from the best linear fit through the initial region of the stress-strain curve. Some typical stress-strain curves are shown in the appendix. Instrument compliance was measured and the apparent modulus was found to be approximately 2 percent lower than the true modulus. Samples that exhibited grip failure were omitted from the tenacity and ultimate elongation results. Each tensile property was averaged over nine tests and performed at ambient conditions in the laboratory. Standard deviations ranged from 5 to 10 percent.

2.3.4 Rheological Measurements

Steady state shear flow measurements were performed on a Rheometrics Mechanical Spectrometer (RMS-800) using a parallel plate geometry. The platens had a radius of 12 mm and a separation distance of 1mm. Temperatures between 270°C and 290°C were investigated at a shear rate of 1 rad/sec. Experiments were performed on ground powders prior to extrusion. All test samples were dried under vacuum at 130°C for 24 hours and then fabricated into 24 mm diameter disks by compression molding at 275°C. Samples were equilibrated at each temperature for 2 minutes prior to measurement and kept under a continuous dry nitrogen purge.

2.3.5 Thermal Instability

Shrinkage experiments were performed by placing the fibers in a convection oven preheated to 190°C for 15 minutes. Prior to heating the fibers were conditioned for 24 hours at 21°C and 68 % relative humidity. The sample lengths before and after heating

were determined at ambient temperature by straightening the fibers with a small load and measuring the initial (L_0) or final (L_1) length respectively. All samples were approximately 20 cm in length before testing. After removal from the oven, the fibers were reconditioned for one hour and the resultant dimensional changes determined. The free shrinkage was computed as

$$[\%] = (L_0 - L_1)/L_1 * 100.$$

Shrinkage values were averaged over 5 measurements.

To measure the development of shrinkage stresses, force-temperature experiments were carried out using a TA Instruments thermal mechanical analyzer. This technique applies a constant strain and measures the development of thermal stresses with temperature change. The fibers were placed in the TMA and an initial strain of 0.05% imposed on the samples. The temperature was then increased at 5°C/min. to 190°C and the resultant load monitored. After being held at 190°C for 15 min., the fiber was slowly cooled to room temperature and the final shrinkage stresses at 190° and 30°C recorded.

2.3.6 Morphology

The morphology of the blends was investigated by optical microscopy (OM) and scanning electron microscopy (SEM). Fiber cross sections were prepared by mounting the samples in an epoxy matrix and either fracturing or cryomicrotoming the sample after cooling in liquid nitrogen. All SEM samples were mounted on aluminum stubs, sputtered with gold using an SPE Sputter Coater, and characterized using a JEOL [JSM-35C] scanning electron microscope. An accelerating voltage of 20 kv was used. An Olympus microscope equipped with a Linkam hot stage was used for observing the blends before and after processing.

2.4 Results and Discussion

2.4.1 Thermal Behavior

The wt. % rod content and thermal transitions for each of the novel TLCP's are shown in Table 2.1. All of these systems exhibit crystal to nematic transitions significantly lower than commercially available TLCP's. For instance Vectra®, a TLCP commonly blended with engineering thermoplastics, has a crystal to nematic transition at 280°C [21]. Lowering the temperature needed to induce the nematic phase reduces the likelihood of thermal degradation and permits a greater degree of processing flexibility in these systems. It is also important that the new TLCP's form anisotropic melts in the temperature range that the PET is melt processed, since many of the processing and mechanical advantages associated with these blends are attributed to the nematic state of the liquid crystalline component [22-24].

Table 2.1. The thermal characteristics and wt. % mesogen content for each copolymer.

	T_m (°C)	lc→lc (°C)	T_d (°C)	Wt. % Mesogen
PME-b-PET (6:6)	224	----	300	40
PME-b-PBT (6:6)	202	----	334	38
PBEM	236	----	348	67
Rnd Copoly (6:10:4)	200	267	325	----

The PBT and PET alternating block copolymers have a single melting transition (T_m) at 202°C and 224°C respectively. Above this transition the polymers exhibit a nematic texture until their thermal degradation point. Although these TLCP's have similar chemical structures and rigid rod contents, approximately 40 wt. %, the initial transition points are 22°C different. This behavior suggests that the nonmesogenic units in these

polymers have a significant effect on the thermal behavior of the block copolymer. This is also apparent when comparing the degradation points of these polymers. The PME-b-PET alternating block copolymer had a degradation temperature (T_d) of 300°C in air, which was 34°C lower than the PME-b-PBT system. The large difference is probably due to a higher concentration of end groups in the PME-b-PET sample since PET should be thermally stable.

Compared to the alternating block copolymers, the PBEM liquid crystalline polymer has a higher rod content, i.e. 67 wt. %. Consequently this material had a higher initial transition (T_m) and degradation temperature (T_d) i.e. 236°C and 348°C respectively. The polymer did not exhibit an isotropic phase prior to decomposition. A large nematic window, approximately 100°C, permits a wide range of processing conditions and applications to be studied. Thus blends can be processed under conditions that are optimum for the matrix component while remaining within the nematic regime of the TLCP.

The random copolymer had the lowest initial transition (T_m) at 200°C. Above this transition optical microscopy revealed a highly birefringent dense nematic thread texture. See figure 2.3. This texture was stable until 267°C when the polymer exhibited a liquid crystal to liquid crystal transition (LC → LC). Above this transition the random copolymer formed a loose nematic texture as shown in figure 2.4. Corresponding to the change in thread texture was a dramatic decrease in the material's viscosity. Although the decrease in viscosity has not been quantified by rheological measurements the difference in flow characteristic was clearly apparent under the optical microscope. The random copolymer was also thermally stable and did not degrade in air until 325°C (T_d). The complex phase behavior of this TLCP is not the subject of this study, however it is known that TLCP's with a similar mesogenic group can exhibit a cybotactic mesophase [25, 26].

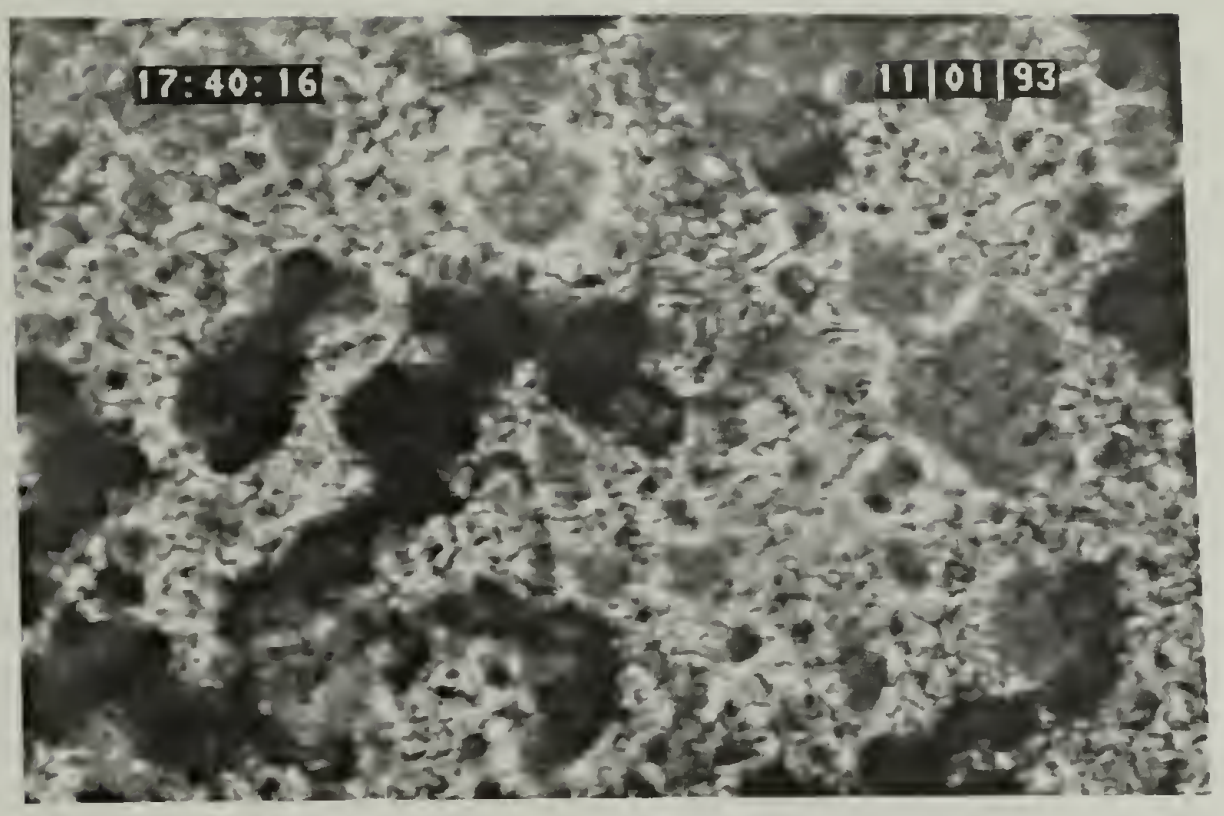


Figure 2.3. The Random Copolymer dense nematic thread texture following melting at 200°C.

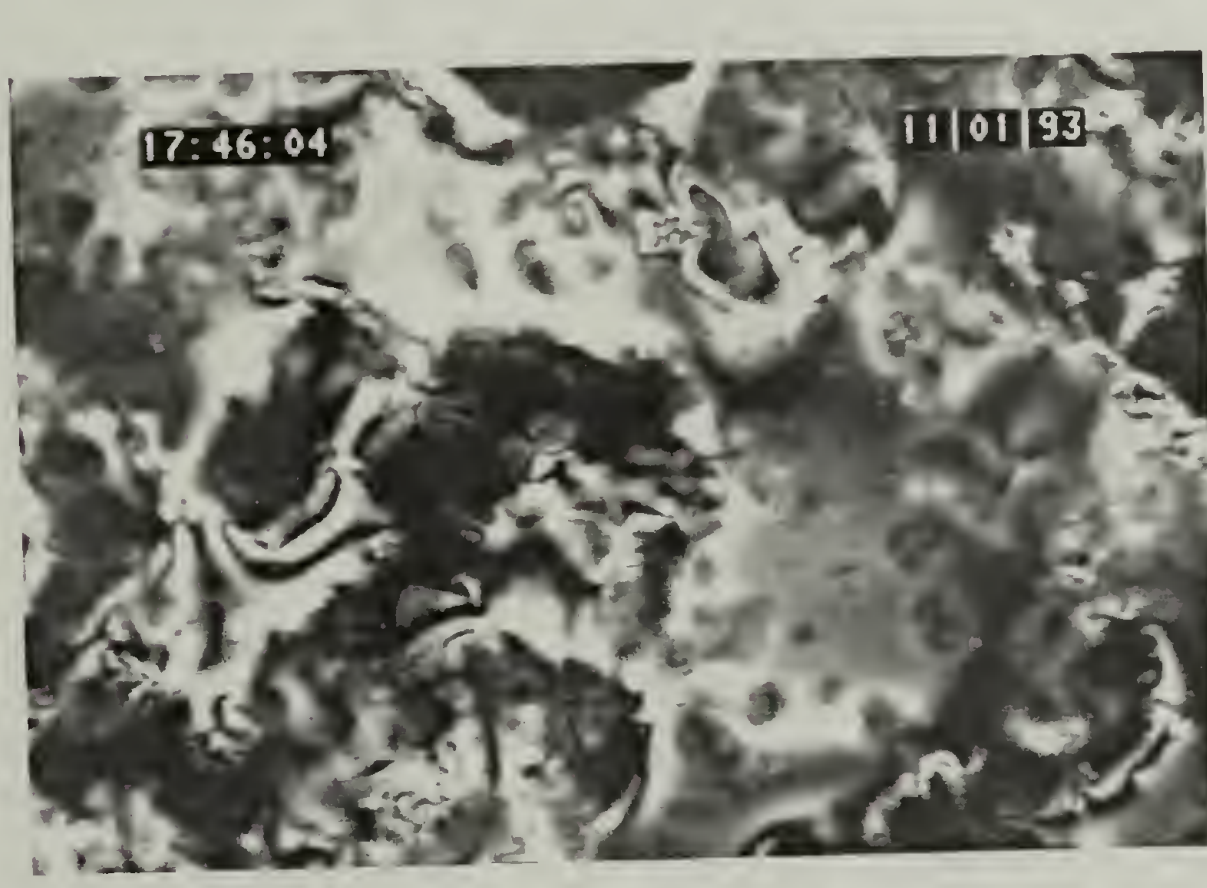


Figure 2.4. The Random Copolymer loose nematic thread texture following the LC → LC transition at 267°C.

2.4.2 PME-b-PET and PME-b-PBT Alternating Block Copolymers

Table 2.2 is a summary of the post-treated fiber tensile properties for blends containing 5, 10 and 20 wt. % of the novel TLCP's. The PET control, spun using a die temperature of 280°C, had a modulus of 17 GPa, an ultimate strength of 1100 MPa, and 9 % strain to break. These are excellent numbers for PET fibers indicating that the spinning and post-treatment processes were sufficiently optimized.

Table 2.2. Tensile properties for blends containing 5, 10, and 20 wt. % TLCP.

	Modulus (GPa)	Ultimate Strength (MPa)	Ultimate Strain (%)
PET Control	17	1100	9
5 % PME-b-PET/PET	19	1100	6
10% PME-b-PET/PET	20	1000	7
20% PME-b-PET/PET	20	700	5
5% PME-b-PBT/PET	18	1100	7
10 % PME-b-PBT/PET	19	1100	7
20 % PME-b-PBT/PET	20	920	7
5 % PBEM/PET	19	1100	7
10 % PBEM/PET	18	1000	8
20 % PBEM/PET	13	600	20
5% Rnd Copolymer/PET	25	1100	7

The tensile properties of the PME-b-PBT and PME-b-PET blends exhibited only minor differences compared to the PET control. Varying the loading level from 5 to 20 % didn't significantly influence the modulus characteristics of either system although the PME-b-PBT system does indicate a gradual improvement in modulus with loading level. At the 20% loading levels for both systems the strength of the fibers were significantly less than neat PET. However, this was not as disappointing as the modulus observations. The ultimate strength and strain to break are not considered crucial when evaluating these materials as potential reinforcing agents for PET. These properties may be influenced by many factors such as the number of fiber defects and molecular weight of the TLCP's. Variables such as these are difficult to optimize when screening many different systems with very small quantities of material. Thus the major criterion for determining a systems effectiveness at this juncture are the fiber moduli since this quantity is less sensitive to processing variables.

Processing of the PME-b-PET blends was difficult due to degradation of the block copolymer. The fibers were processed using a die temperature of 280°C, which is 20°C lower than the degradation point as determined by TGA, but gas bubbles were still readily apparent in the fiber during spinning. This degradation may be responsible for the large drop in tensile strength at 20% loading levels for this system. The PME-b-PBT block copolymer was processable without visible degradation at all loading levels, but significant modulus or strength improvements were not obtained. However, the 10 and 20% fiber blends were stronger than the corresponding PME-b-PET systems. Thus the PBT units increased the thermal stability of the block copolymer without inducing compatibility problems between the components.

Large improvements in mechanical performance were not observed, but processability of the PME-b-PBT blends was good and large scale phase separation was absent. The block copolymer may have provided some compatibility with the PET matrix,

but the incorporation of 50 % flexible moieties may have excessively reduced the polymer's stiffness. In order for an LCP to mechanically improve drawn PET it should have a modulus significantly greater than 17 GPa. This may require block copolymers to have smaller flexible blocks in order to provide a sufficient modulus for reinforcement of the PET.

2.4.3 PBEM

Although PBEM has a higher rod content than the alternating block copolymers, it still did not significantly reinforce the PET fibers. At lower loading levels, 5 and 10 wt. %, the blends exhibited minor improvements in modulus, 18 and 19 GPa respectively. The strength of the 5% system was equivalent to the PET control, 1100 MPa, but the 10% blend showed a 100 MPa reduction in strength. The 20% blend had a significantly lower modulus and strength, 13 GPa and 600 MPa respectively. As indicated by their high ultimate strain, 20 %, these fibers could not be post-treated effectively due to defects and frequent fiber breakage.

Observation of the 20 % as spun PBEM fiber under the optical microscope indicated a skin-core morphology. See figure 2.5. Cracks in the liquid crystalline skin are visible in the fiber at a magnification of 200X but become more apparent when examined under cross polars. See figure 2.6. The highly birefringent skin surrounds a less oriented core. The cracks in the skin region may be the result of a large amount of stretching during the spinning process or thermal expansion differences between the components as the fiber cooled. During post treatment the skin region becomes increasingly damaged with large sections lost during the hot drawing step. The final post-treated fiber contained a large number of defects due to inefficient drawing which ultimately resulted in the poor tensile properties.

Figure 2.5. Optical micrograph of the 20% PBEM fiber exhibiting a skin-core morphology (mag. 200X).

Figure 2.6. Optical micrograph of the 20% PBEM fiber exhibiting a skin-core morphology (mag. 200X with cross polars).

The development of a skin-core morphology is generally observed when the viscosity ratio of the matrix polymer to the dispersed phase is large [24]. The low viscosity liquid crystal migrates to the surface forming an LCP rich skin region. These observations indicate PBEM may have potential applications as a processing aid for PET. Blending a low viscosity LCP with an isotropic polymer often decreases the viscosity of the isotropic polymer. The lower viscosities of these blend systems often allows them to be processed more easily than the neat thermoplastic.

The steady shear viscosities for blends containing 2.5, 5 and 10 wt. % PBEM show almost a 75% reduction in viscosity compared to the PET control at 270°C. See figure 2.7. Viscosity reduction in the blends appears to be independent of loading level i.e. the 2.5 % blend was just as effective as the 10 % blend at lowering the viscosity of the PET. This indicates the reduction mechanism may be a surface phenomena since it is unlikely that a bulk effect would be concentration independent. Immiscibility of the two components combined with a high viscosity difference could promote the formation of a surface region rich in PBEM reducing the measured viscosity. The extent of the concentration independence is unknown since blends containing less than 2.5 wt. % PBEM have not been investigated. This experiment was performed at a shear rate of 1 rad/sec which is significantly lower than that experienced under practical processing conditions, however, most investigators have observed improved viscosity reduction at higher shear rates [11, 27-30].

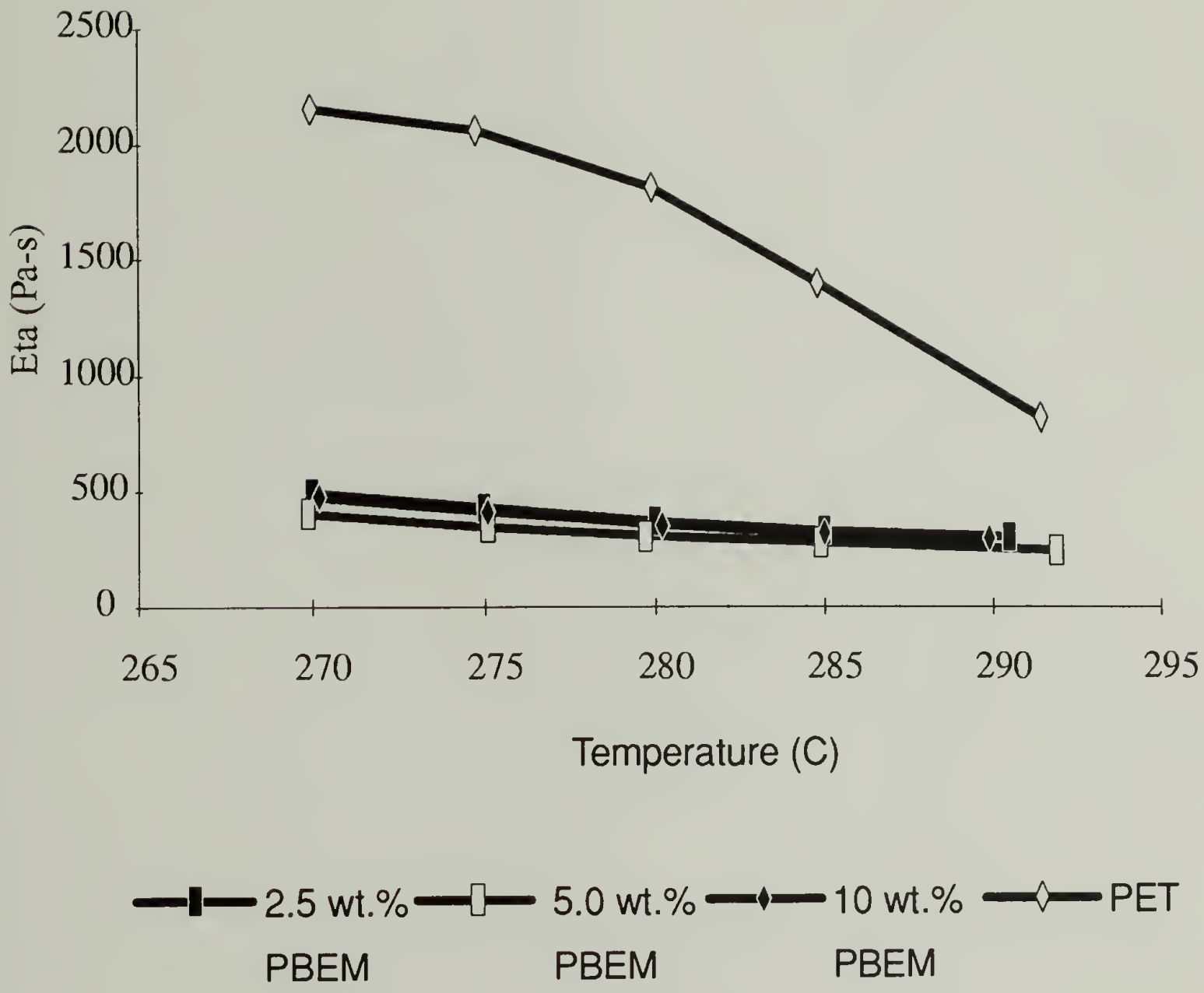


Figure 2.7. Steady shear viscosities of the PBEM blends as a function of LCP content.

Increasing the temperature of the rheometer to 290°C reduced the magnitude of the viscosity difference between the blends and the PET control, but the systems were still concentration independent. Thus adding a small percentage of PBEM to PET could permit processing at lower temperatures without hurting fiber performance. As shown previously the tensile properties of the 5 wt. % blend were equivalent or slightly improved compared to neat PET. Reducing the processing temperature to 270°C or lower would decrease the threat of polymer degradation and save energy.

2.4.4 Random Copolymer

Fiber containing 5 % of the random copolymer had the best mechanical performance. The post treated 5 % random copolymer blend had a 25 GPa modulus, an 1100 MPa ultimate strength, and 7 % strain to break. This corresponds to a 50% increase in fiber stiffness with no change in ultimate strength compared to the PET control. The strain to break was decreased slightly from 9 to 7 % but this was not considered significant. A blend containing 10 % random copolymer was spun but the fibers were intractable during the post-treatment process. Due to the problems associated with processing the 10 % system a 20 % blend was not attempted.

Although the systems became intractable at the higher loading levels the modulus improvement in the 5 % system was impressive. Assuming the fiber contained 95 volume percent PET, a rule of mixtures relationship would imply that the random copolymer has a modulus of approximately 175 GPa. This was surprising and unlikely since it's approximately 25 GPa greater than stiffness values obtained for heat treated aramid PPTA fibers (125 GPa). The modulus of the random copolymer should be lower than the all aromatic aramids since flexible moieties were incorporated into the main chain.

If the random copolymer had a modulus of 175 GPa, dramatic improvements in the as-spun moduli would also be expected since as-spun PET only has a modulus of 2 GPa. Several investigators have shown mechanical reinforcement of extruded or injection molded PET using the commercial TLCP Vectra [31-33]. The as-spun moduli for fiber blends containing 2, 5, 6, 8, and 10 wt. % random copolymer are show in figure 2.8. This data shows a gradual improvement in blend modulus from 2 to 3 GPa as the loading level was increased from 2 to 6 %. Above 6 % a plateau is observed and the blend moduli remained constant as the LCP concentration was increased to 10 %. Thus the random

copolymer does not appear to mechanically reinforce as-spun PET significantly, particularly when compared to the post-treated samples. These results indicate the random copolymer either modified the behavior of the PET matrix in some fashion or was dramatically improved by the post-treatment process. For instance if the LCP induced an increase in PET orientation or crystallinity during post-treatment an improvement in performance could be obtained strictly on the basis of an enhanced matrix. Conversely if the drawing performed during post-treatment increased the aspect ratio and orientation of the LCP the improved properties may have permitted mechanical reinforcement of the fiber.

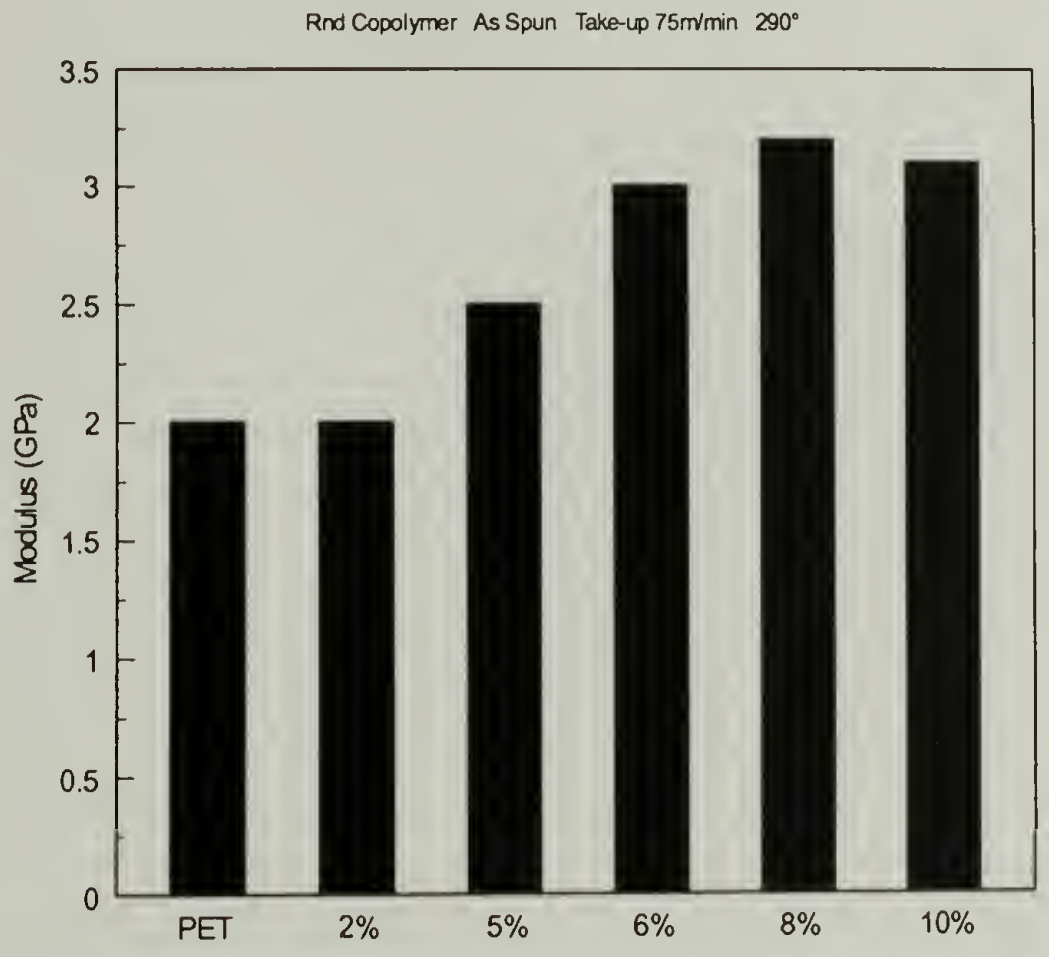


Figure 2.8. As-spun moduli for the Random Copolymer blends as a function of concentration.

DSC heating scans were performed on the powders prior to extrusion. The samples were heated to 300°C to remove any prior thermal history and quench with liquid nitrogen. The results of the second heating runs for the 5 and 10 % random copolymer blends were compared to a PET control in figure 2.9. Table 2.3 gives the relevant

numerical data. The heats of fusion and crystallization for the blends have been normalized with respect to PET content.

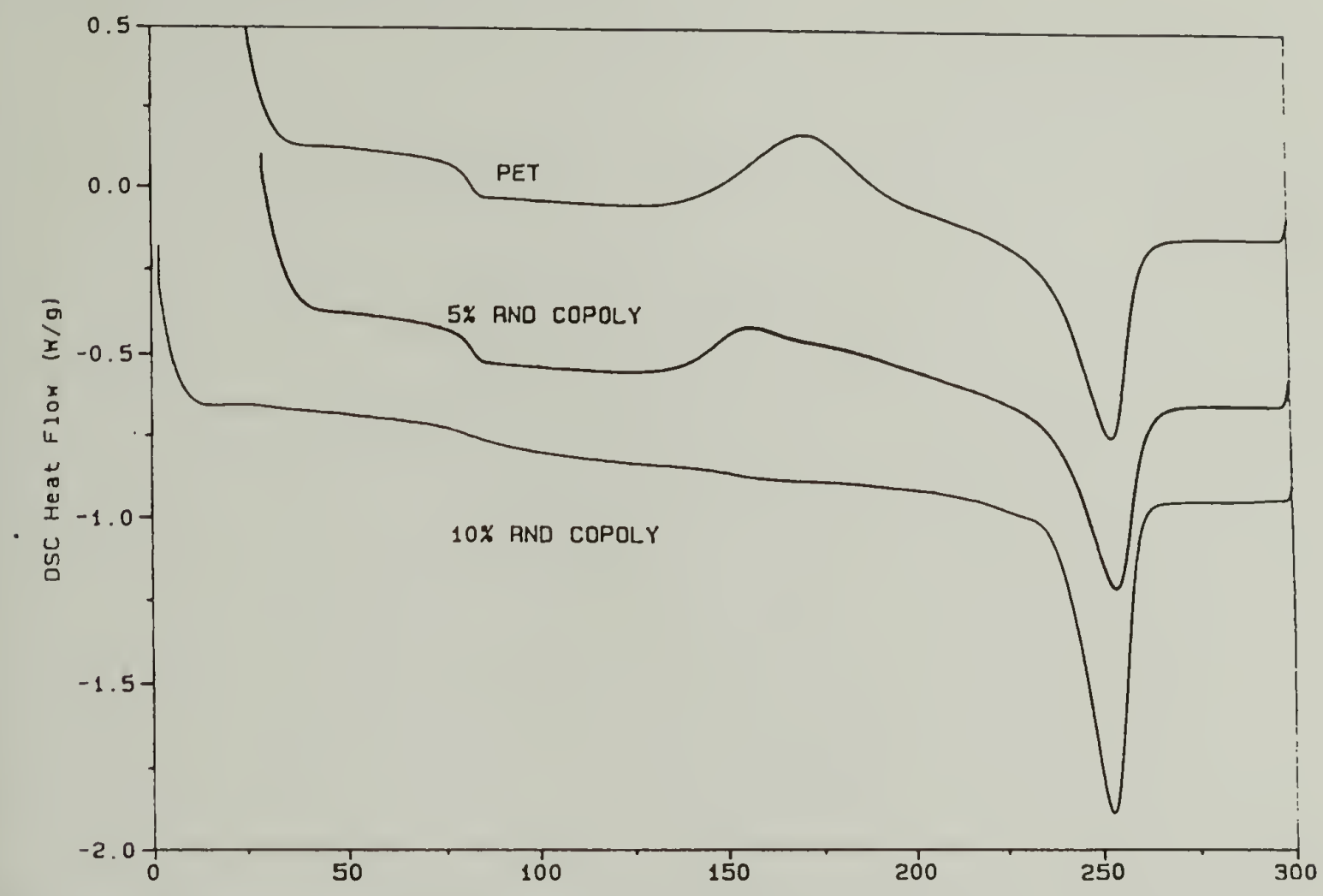


Figure 2.9. DSC heating scans as a function of Random Copolymer concentration.

Table 2.3. Numerical data determined from DSC measurements of PET blend systems.

	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PET	82	171	23	253	29
5% Random Copolymer	83	157	16	254	33
10% Random Copolymer	81	----	----	253	38

The blends show significant deviations from the PET control. The PET control had a Tg at 82°C while the 5 and 10 % blends had Tg's of 83°C and 81°C respectively. The Tg's of the blend systems are essentially identical to the PET control indicating that either the Random Copolymers has a similar glass transition temperature or that little no

interaction has occurred between the two materials. However the most dramatic differences are observed in the cold crystallization and melting transitions. The PET control had a cold crystallization peak at 171°C with a heat of crystallization of 23 J/g. This transition was shifted down to 157°C in the 5 % system and the heat of crystallization was reduced to 16 J/g. This effect was more pronounced for the 10 % system which didn't exhibit any cold crystallization prior to melting. Thus the random copolymer was able to induce a significant amount of crystallization during the quench indicating it is an efficient nucleating agent for PET. The ability for LCP's to perform as nucleating agents has been observed in several other systems [23]. In addition to the absence of cold crystallization, the 10% system had a heat of fusion of 38 J/g compared to 29 J/g for the PET control. Thus the LCP may have also increased the overall amount of PET crystallinity. This is an important observation because an increase in the amount of fiber crystallinity could result in improved performance.

The ability to post-treat the random copolymer blends varied depending on the concentration of LCP incorporated. The results are shown in figure 2.10. The 2 % system could be drawn easily but the tensile properties were identical to the PET control except for a 100 MPa reduction in strength. The 5 % system was also easily drawn yielding significant enhancement as discussed previously while the 6 % system could only be drawn with difficulty. After cold drawing the 6 % system had a significant number of defects preventing a continuous hot drawing process. These fibers had to be hot drawn by hand and the resultant tensile performance was significantly lower than the PET control. Results for the 8 and 10 % are not available since it was not possible to post-treat these blends without fiber breakage.

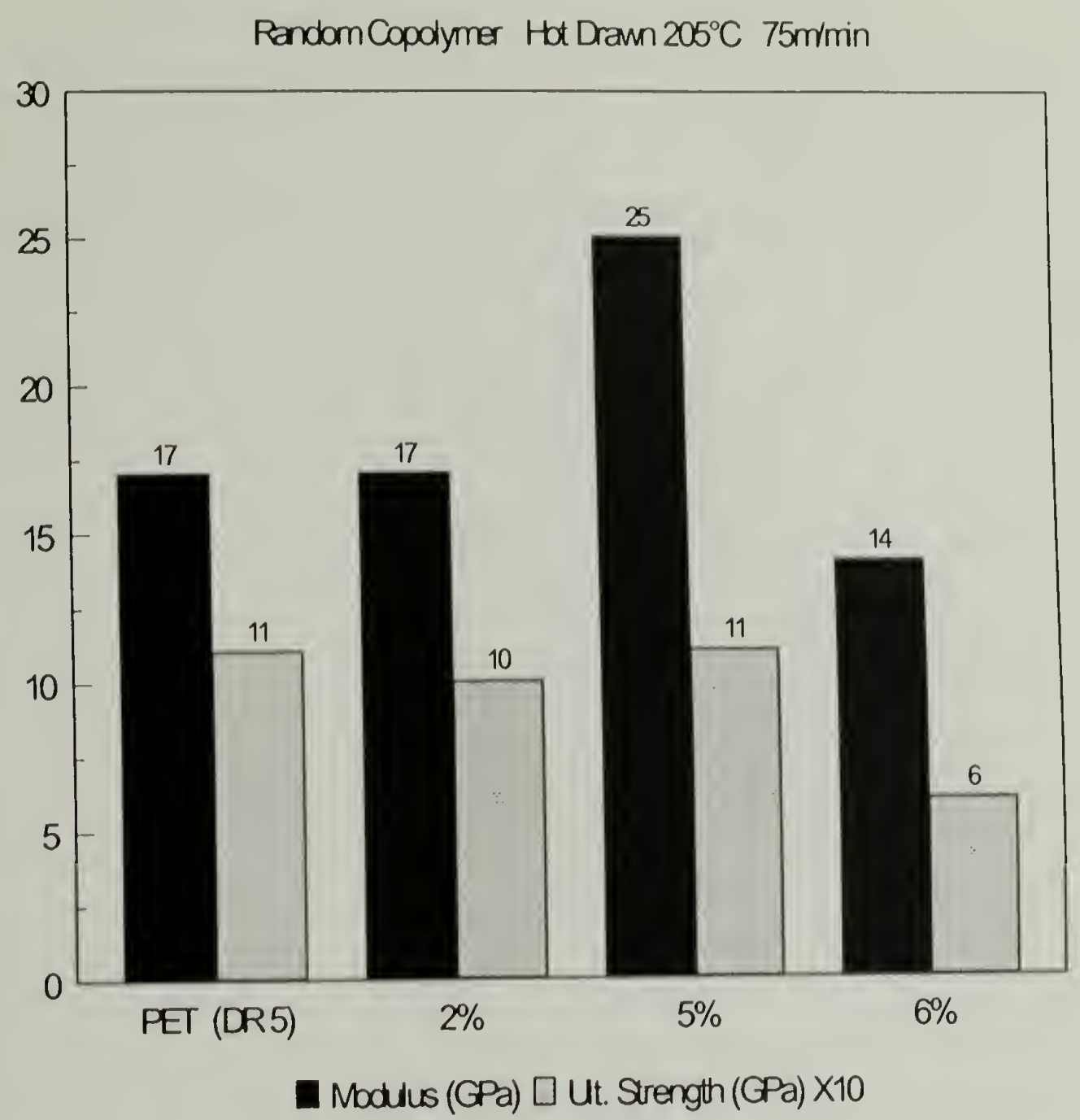


Figure 2.10. Post-treated tensile performance of the Random Copolymer blends as a function of concentration.

These results indicate it is unlikely that the orientation and the aspect ratio of the random copolymer phase could be improved during drawing steps. If significant deformation of the LCP were possible in the 5 % blend, deformation should also occur at higher concentrations which was clearly not possible. Furthermore the random copolymer has shown the ability to affect the crystallization behavior of PET. Thus it is not unreasonable to suggest that the LCP could be modifying the PET matrix in the fibers. Increasing the amount of PET crystallinity that develops during drawing could improve the tensile behavior of the fiber. This phenomena could also be concentration dependent

since the extent of PET modification could be determined by the amount, the orientation, or the domain size of the copolymer phase within the fiber [34]. Thus a critical LCP loading level may be necessary before modification of the PET is sufficient to improve performance. In addition, higher loading levels could increase the LCP domain size or induce premature crystallization of the PET matrix preventing efficient drawing behavior

Due to the interesting phase behavior of the random copolymer and the property enhancements obtained with the 5% system, the spinning of this blend was investigated in further detail. An evaluation of three different die zone temperature settings can be seen in figure 2.11. All of these system exhibited higher moduli values compared to the PET control, but the fibers spun at 290°C showed the greatest improvement, attaining a modulus of 25 GPa with no decrease in ultimate strength. The fibers spun at 260°C had a modulus of 21 GPa and a strength equivalent to the PET control. The temperature of the die zone for this spinning run was below the liquid crystal to liquid crystal transition for the random copolymer. Spinning below this temperature obviously has a significant effect on the final fiber properties but the reason for this is presently unknown. The fibers spun at 310°C had a slightly lower modulus, 19.5 GPa, and a small reduction in ultimate strength. The cause for the decrease in stiffness and strength is unknown but 310°C is close to the degradation temperature of the liquid crystal and some degradation of the polymer may have occurred. In addition, at temperatures greater than 300°C chemical reactions such as transesterification can take place very rapidly causing changes in the system.

Thus the processing window for these blends appears to be between 260°C and 310 °C. Due to the relatively small quantities of available material further optimization of the processing conditions was not possible. However, if further process optimization was possible even greater improvement in fiber performance would be expected.

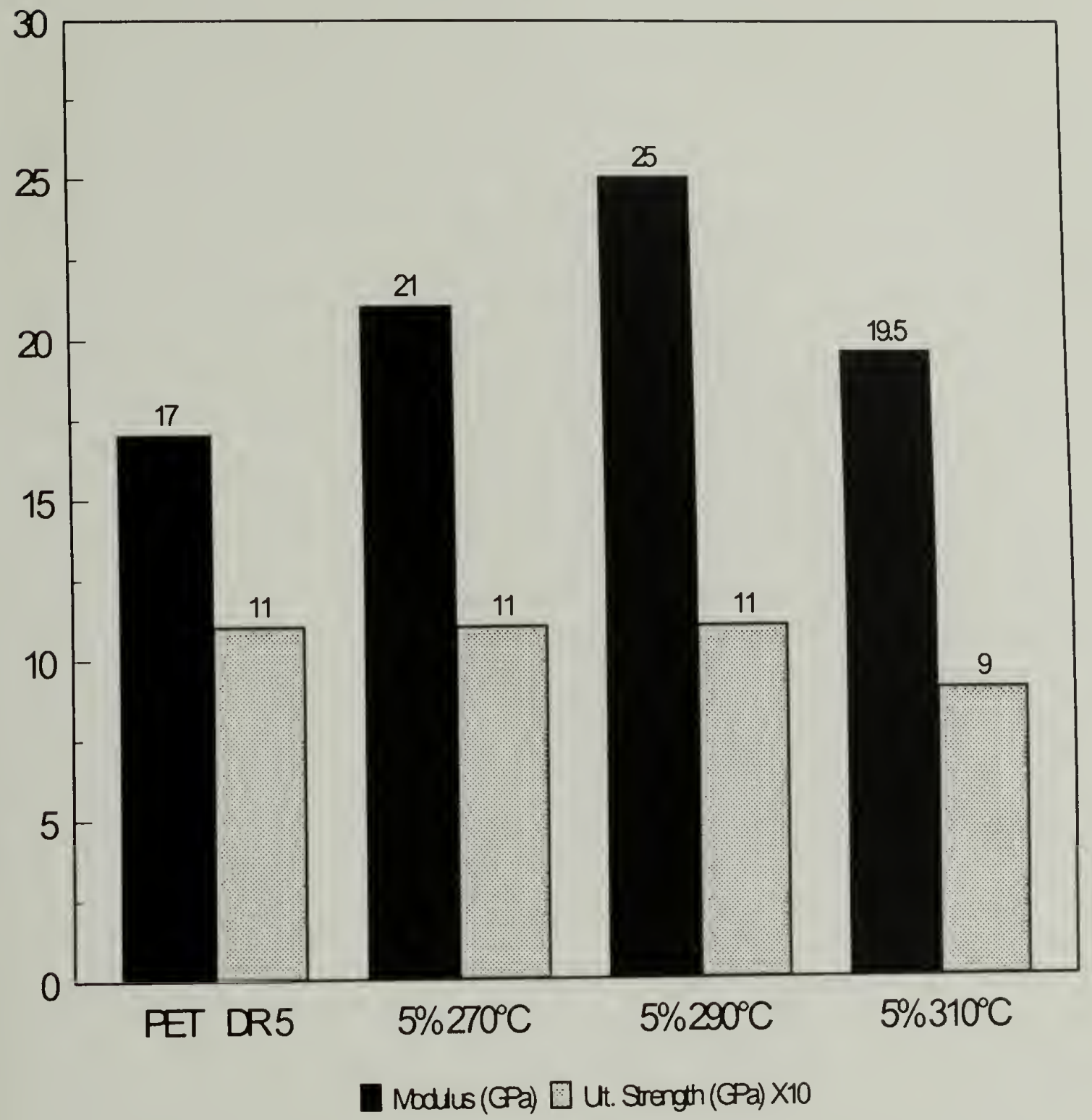


Figure 2.11. Tensile performance of the 5% Random Copolymer system as a function of the die zone processing temperature.

The effect of increasing draw ratio on mechanical properties was examined for the 5% blend spun at 290°C as seen in figure 2.12. As the draw ratio was increased the modulus and ultimate strength improved. The modulus increased from 14 to 25 GPa and the ultimate strength improved from 500 to 1100 MPa. These increases in modulus and strength were accompanied by a corresponding decrease in the ultimate elongation of the

fibers from 33 to 7 %. The continuous increase in modulus and strength indicates that these fibers have not been excessively drawn. Excessively drawn fibers exhibit increases in stiffness but with a corresponding drop in the ultimate strength of the fiber. The decrease in strength is associated with the breaking of the load bearing tie molecules.

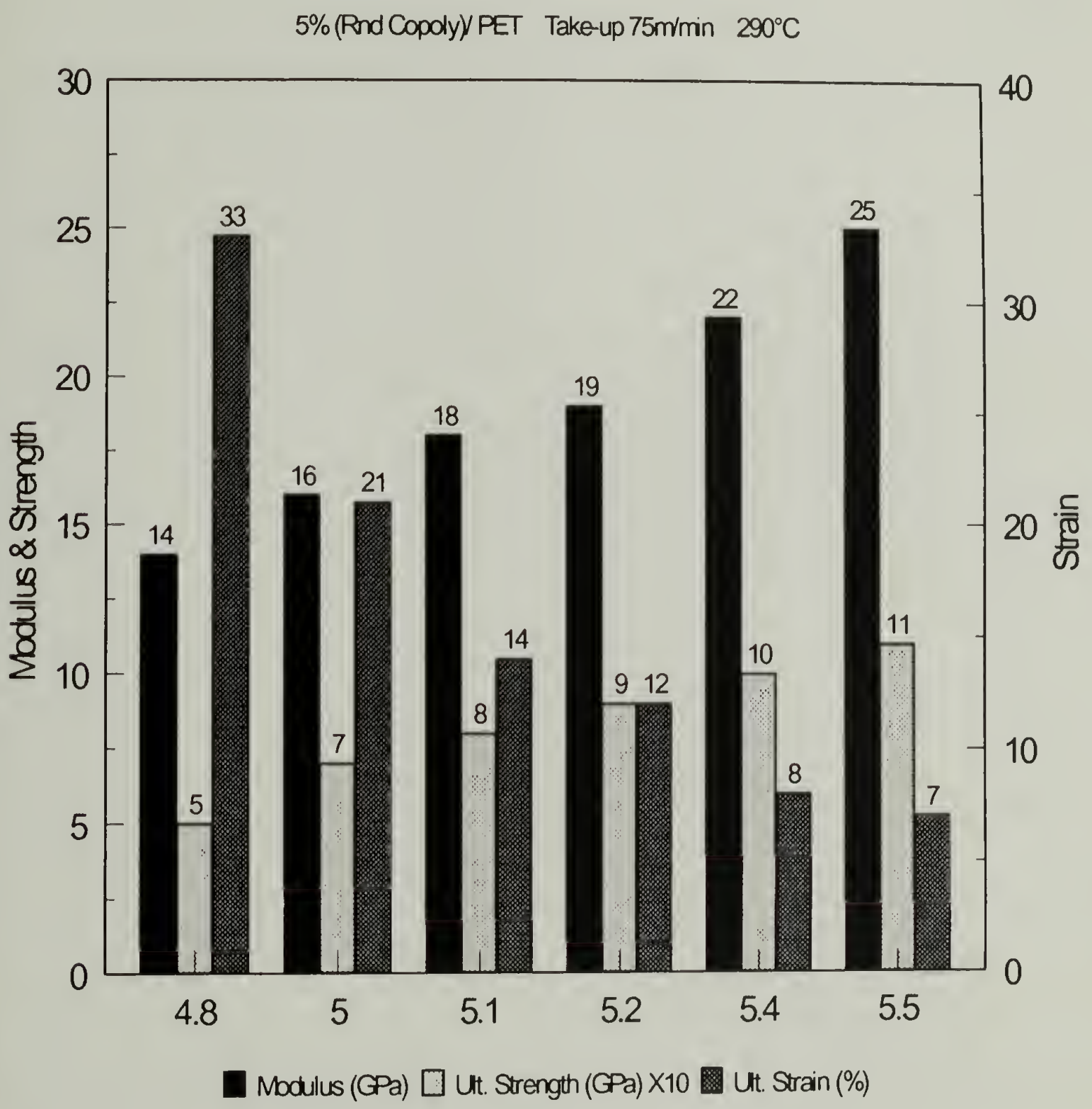


Figure 2.12. Mechanical performance of the post-treated 5% Random Copolymer system as a function of final draw ratio.

2.4.5 Dimensional Instability

Commercial thermotropic liquid crystals are dimensionally stable and have been used in injection molding applications where tight tolerances and no part warpage are desired. Nicolais and coworkers [35] have also shown that blending polymeric thermotropic liquid crystals with polystyrene can be very effective in improving the dimensional stability of the thermoplastic. Thus it was hoped that the addition of 5 % random copolymer to PET would result in fibers with superior dimensional stability compared to neat PET.

The dimensional instabilities of the 5 % fibers spun at 290°C were measured using free shrinkage and force temperature experiments. The dimensional instability versus draw ratio is shown in Table 2.4. The free shrinkage of the fibers varied from 6 to 10% as the draw ratio was increased. Corresponding to the increase in free shrinkage was an increase in the shrinkage stresses. Comparison of the 5% blend having a draw ratio of 5.4 with the PET control reveals that similar shrinkage stresses result in equivalent dimensional changes. Thus the addition of 5% LCP does not appear to improve or detract from the fiber's thermal performance.

Table 2.4. Dimensional instability of the post-treated 5 % Random Copolymer system as a function of draw ratio.

Draw Ratio	Free Shrinkage (%)	Shrinkage Stress 190°C (MPa)	Shrinkage Stress 30°C (MPa)
PET = 5	9	80	45
5% Rnd Copoly = 4.8	6	25	11
5% Rnd Copoly = 5.0	6	28	13
5% Rnd Copoly = 5.1	8	50	27
5% Rnd Copoly = 5.2	8	70	40
5% Rnd Copoly = 5.4	9	84	45
5% Rnd Copoly = 5.5	10	86	42

2.4.6 Morphology

Cross-sections of 5% as-spun fibers, observed using scanning electron microscopy, showed a distinct two phase morphology with the TLCP phase elongated into fibrils. See figure 2.13. The fibrils varied in diameter form 0.2 to 0.4 microns and were uniformly dispersed throughout the PET matrix. The presence of a fibrillated LCP phase indicates that the temperatures selected for processing were reasonable although they could not be optimized.

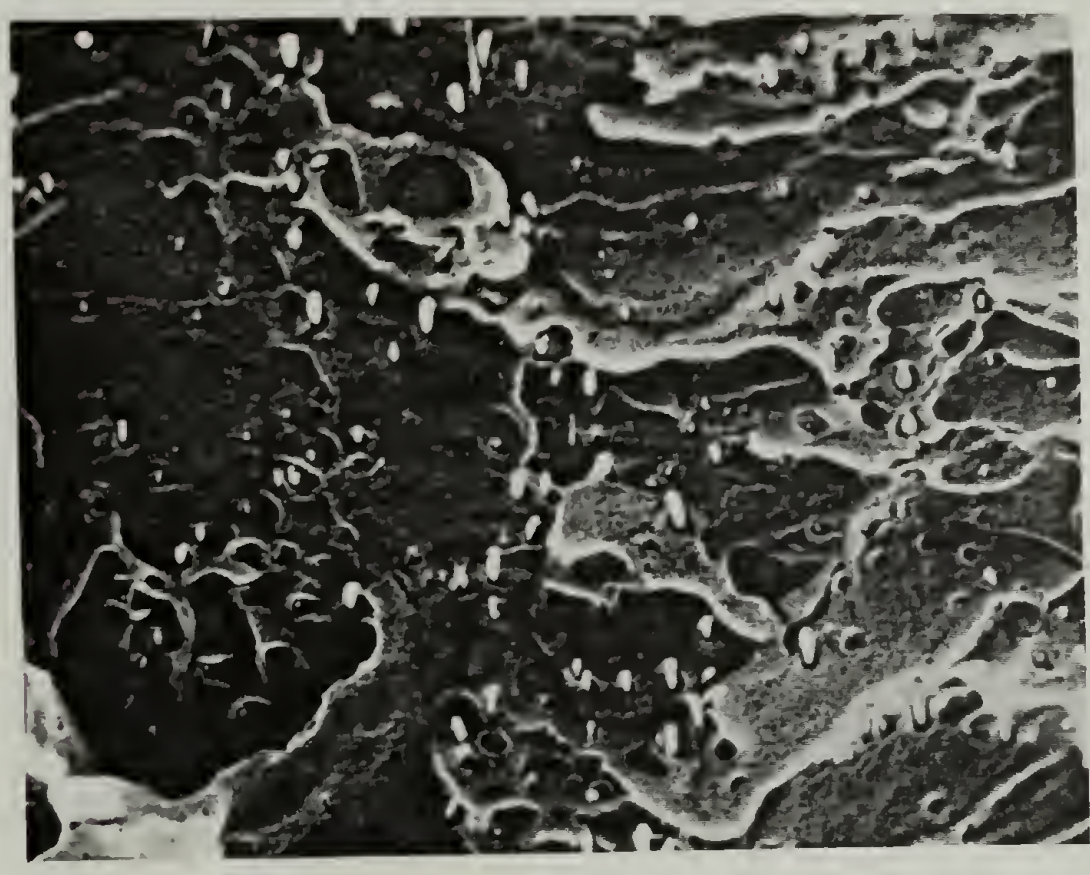


Figure 2.13. An SEM cross-section of the 5% Random Copolymer as-spun fiber.

Although DSC does not indicate significant interaction between the random copolymer and PET, gross incompatibility is also absent. There was no indication of a skin core morphology and phase separation between the components was limited to sub micron LCP domains. Observation of the fiber cross-section at a higher magnification, see figure 2.14, did not yield any evidence of adhesion between the phases. This observation

could be an artifact of the sample preparation technique. It is well known that cracks tend to propagate along interfaces at liquid nitrogen temperatures. Many of the fibrils showed evidence of fracture indicating that the aspect ratio of the fibrils was enough for frictional forces to be significant. This could be the result of thermal expansion differences between the components causing a strong mechanical interaction between the two phases.

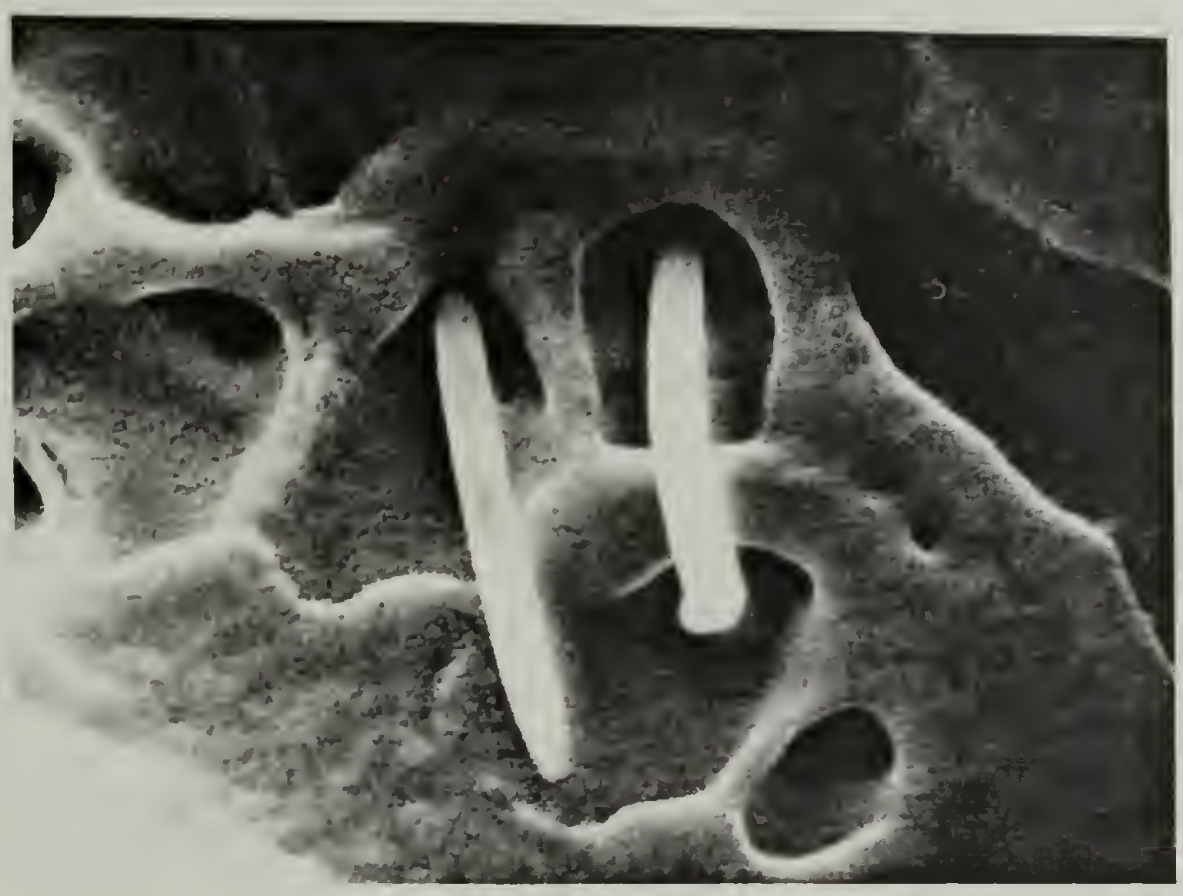


Figure 2.14. An SEM cross-section of the as-spun 5% Random Copolymer fiber magnified 30, 000 times.

A longitudinal fiber cross section was prepared by mounting a sample in an epoxy matrix and cryomicrotoming at -55C. Observation of the fiber under the optical microscope 500 times, figure 2.15, shows the knife cut across the fiber and evidence of elongated fibrils oriented along the fiber axis. Fibrils with aspect ratios ranging from 20 to 200 could be easily found assuming a diameter of 0.4 μm. This should be considered a minimum aspect ratio range since the fiber was not cut perfectly horizontal but was slightly off axis. Furthermore the maximum observed fibril diameter was assumed.

Figure 2.15. Longitudinal cross-section of the as-spun 5% Random Copolymer fiber observed with optical microscopy.

2.5 Conclusions

The objective of this study was to blend PET with novel thermotropic liquid crystalline polyesters to improve fiber performance or processability. Several different TLCP architectures were screened in an effort to determine the optimum molecular architecture necessary for fiber enhancement. The TLCP's were specifically tailored to be compatible with the PET matrix. Improving blend compatibility should permit fiber post-treatment and increase the interfacial adhesion between the blend components.

The PME-b-PET and PME-b-PBT block copolymers did not significantly reinforce the PET fibers, but minor improvements in fiber modulus were apparent in both systems. The blends could also be processed and post-treated at the 20 % loading level, indicating

some compatibility was attained. The fact that only moderate modulus improvements were observe may have been due to the incorporation of 50 wt. % flexible moieties into the main chain. This may have reduced the moduli of the block copolymers to such an extent that significant reinforcement was not possible at low loading levels.

The incorporation of either PET or PBT flexible moieties into the block copolymer did not affect the reinforcement characteristics. The tensile properties of the two block copolymer systems were essentially identical. This is significant because the PME-b-PBT copolymer had higher molecular weight, better processability, and greater thermal stability.

Although the PBEM material should be stiffer than the block copolymers, significant modulus improvement was not observed. Furthermore as the weight percent LCP was increased from 5 to 20 % a dramatic skin-core morphology developed indicating incompatibility between the blend components. However, steady shear viscometry showed that PBEM has the potential to be an excellent processing aid for PET. At loading levels as low as 2.5 wt. % the blend exhibited a 75% reduction in viscosity at 270° C. This could permit processing at lower temperatures reducing the threat of degradation. The spinning of higher molecular weight PET may also be possible.

The random copolymer system was found to have improved the mechanical properties compared to neat PET fibers. Fibers containing only 5 % TLCP exhibited a 50 % increase in modulus, while maintaining an ultimate strength equivalent to the PET control. The mechanism of reinforcement is unclear but evidence indicates the LCP is modifying the PET matrix. Scanning Electron Microscopy observations of fractured fiber cross sections revealed that the TLCP phase was elongated into fibrils. The fibrils were 0.2 to 0.4 μm in diameter and uniformly dispersed throughout the PET matrix. The spinning temperature and draw ratio were critical processing parameters that dramatically affected mechanical properties and thermal behavior. The thermal behavior of the 5 %

system, as determined by free shrinkage and force-temperature experiments, was similar to the PET control.

Although the mechanism of improvement is currently unknown, it is obvious that the addition of mesogenic block copolymers can significantly enhance the performance of PET. This is an important accomplishment since PET fibers must undergo extensive drawing in order to attain the necessary performance characteristics. At comparable loading levels, conventional thermotropic LCP's have not exhibited any significant PET reinforcement characteristics. Thus the potential of these materials is high particularly since the processing conditions could not be optimized due to material constraints. By continuing to modify the molecular architecture and processing of these block copolymers, greater improvements in fiber performance are expected.

2.6 References

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CHAPTER 3

PET BLENDED WITH ALTERNATING TLCP BLOCK COPOLYMERS CONTAINING PBT FLEXIBLE MOIETIES

3.1 Introduction

In-situ composites are formed by the inclusion of a liquid crystalline rigid rod polymer in an isotropic matrix. Kiss [1] used the term in-situ composites for these materials since the reinforcing species is not actually present in the starting materials, but comes into existence during processing. These systems may provide good mechanical performance while preventing technical difficulties associated with the presence of a solid filler. Solid fillers such as chopped glass fibers can cause significant wear on processing equipment, increase the molten polymer viscosity and pose difficulties in compounding. Thus it would be highly desirable to develop in-situ composites since the reinforcing component develops upon solidification into highly oriented and rigid inclusions.

Thermotropic liquid crystalline polymers (TLCP's) are currently the preferred reinforcement material for designing in-situ composites. The large scale interest in thermotropic systems is due to their ability to be used with conventional melt processing techniques and equipment without expensive and potentially hazardous solvents. Thermotropic polymers can form highly oriented, anisotropic fibrous domains or inclusions in a matrix polymer when processed under the appropriate conditions. Due to their potential to develop high strength and stiffness, these fibrous inclusions may act as a reinforcement agent, much like chopped glass. Furthermore TLCP's offer a range of other interesting properties such as low viscosity, low thermal expansion in the direction of orientation and chemical resistance. Thus TLCP's blended with engineering

thermoplastics could impart thermal stability or function as a processing aid [2-5]. Most of the work to date has centered on melt blending commercial thermotropic copolyesters, such as Vectra®, Xydar® or X7G® with engineering thermoplastics, e. g. poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT), as well as polycarbonate (PC), poly(ether ether ketone) (PEEK) and Nylons. Several reviews on the subject have been published recently [6-8].

A degree of compatibility between TLCP's containing ethylene terephthalate units with PET and polycarbonate has been observed, but the majority of thermoplastics have been found to be incompatible with TLCP's [9, 10]. Incompatibility between blend components is thought to be undesirable since it can result in poor interfacial adhesion and adversely affect the mechanical properties of the system [1, 11, 12]. However, miscibility is also thought to be undesirable for these blends. The existence of a two phase morphology is regarded as necessary in order to obtain the processing and mechanical benefits of the TLCP. Thus a degree of compatibility is desired such that good interfacial adhesion is achieved without sacrificing potential processing and property enhancements. An approach for accomplishing this objective is the use of tailored block copolymers. By incorporating flexible blocks similar to the matrix polymer into the TLCP chain, the interfacial adhesion between blend components should improve and consequently increase mechanical performance.

In this study poly(ethylene terephthalate) (PET) has been blended with several novel thermotropic liquid crystalline polyesters and the physical and mechanical properties investigated. The objective was to determine if properties superior to neat PET fibers could be attained by incorporating a liquid crystalline polyester composed of rigid mesogenic moieties and flexible poly(butylene terephthalate) segments. PBT is miscible with PET and could promote compatibility between the two phases.

Due to limited amounts of the block copolymers, a screening procedure has been developed to determine if a blend system exhibits desirable characteristics. Compositions

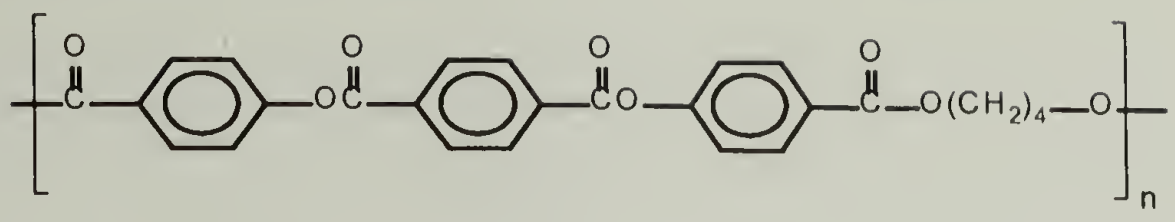
varying from 5 to 20 wt.-% LCP are commercially interesting and therefore evaluations focused on this range. Fibers are prepared by melt extrusion followed by cold and hot drawing. The fibers are tested for tensile performance, dimensional instability (shrinkage), and the development of shrinkage stresses.

3.2 Materials

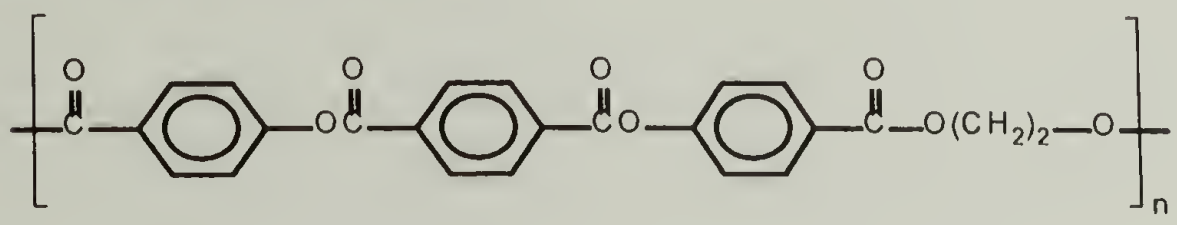
The thermotropic LCP's used in this study are a group of novel block copolymers kindly synthesized by Drs. Lenz and Kantor's group at the University of Massachusetts, Amherst [13]. The LCP's are segmented block copolymers consisting of rigid-rod, diad, and flexible coil segments. Figure 3.1 shows a schematic of the general structures used in this study. The mesogenic blocks are composed of either poly(tetramethylene-4,4' terephthaloyl dioxydibenzoate) (Triad4) or poly(dimethylene-4,4' terephthaloyl dioxydibenzoate) (Triad2) units. The flexible coil segments are poly(butylene terephthalate) (PBT). Futhermore, due to the reaction scheme chosen to synthesize these copolymers, tetramethylene-4.4' dioxyterephthaloyl benzoate (Diad4) sequences are incorporated between the rigid-rod and flexible coil segments. These diads are known to be mesogenic [14].

Several different copolymer systems have been investigated to determine the optimum molecular architecture necessary for PET reinforcement. Variables that were considered included: block size, rigid-rod content, PBT content, and mesogen rigidity. The molar ratio of the Diad4, Triad, and PBT sequences incorporated into each block copolymer are shown in figure 3.2. For instance the Triad4 (2:4:21) block copolymer has two Diad4 units which separate Triad4 and PBT blocks having segment lengths of 4 and 21 units respectively.

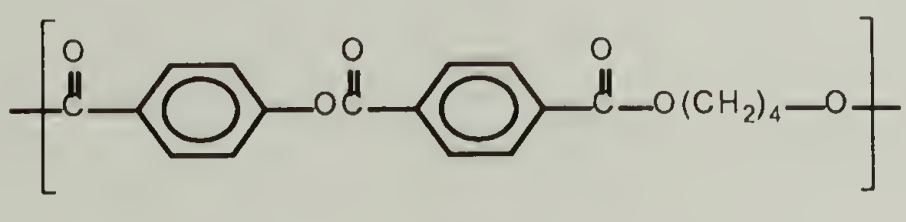
Triad4 Mesogenic Block



Triad2 Mesogenic Block



Diad4 Unit



PBT Flexible Block

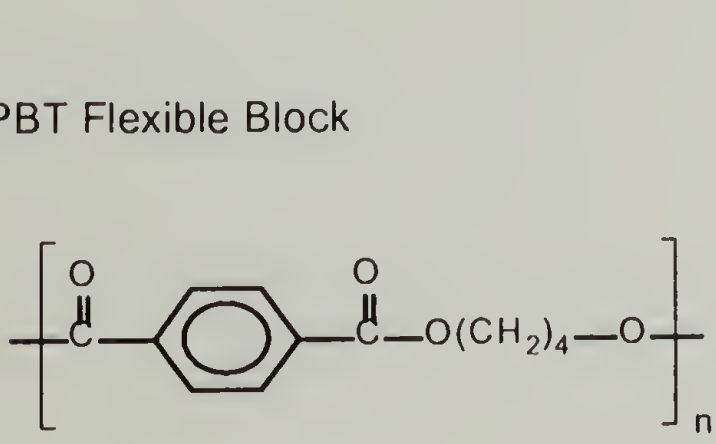


Figure 3.1. The rigid and flexible moieties incorporated into the alternating block copolymers.

The amount of material available for blending and property determination for each LCP was limited to approximately 7 grams, thus the mechanical properties of the neat copolymers could not be determined.

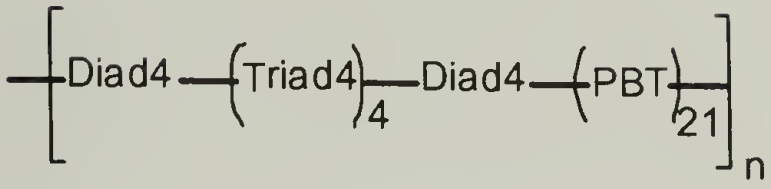
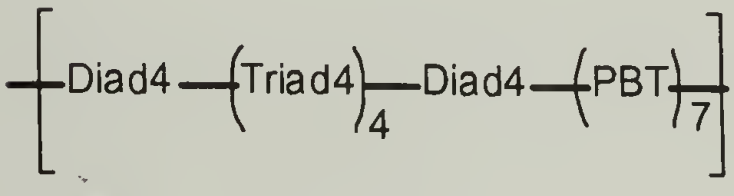
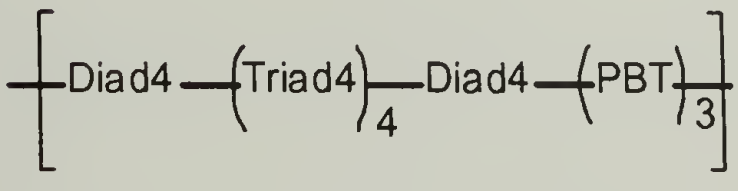
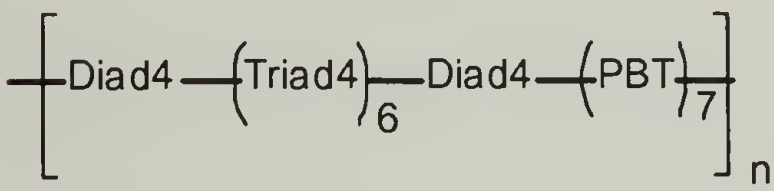
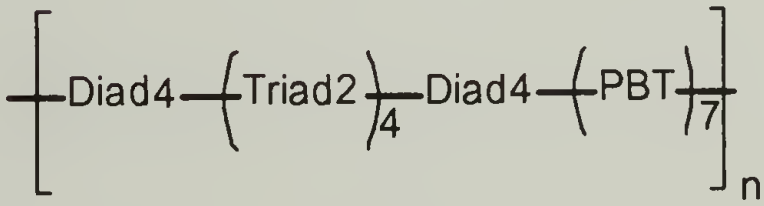
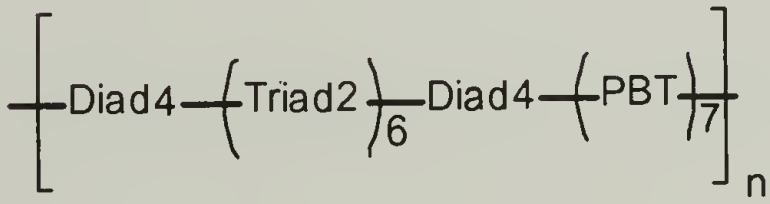
Block Copolymers	Copolymer Structures
Triad4 (2:4:21)	
Triad4 (2:4:7)	
Triad4 (2:4:3)	
Triad4 (2:6:7)	
Triad2 (2:4:7)	
Triad2 (2:6:7)	

Figure 3.2. Schematics of the polymer structures and the molar ratios of mesogenic to flexible moieties incorporated into the alternating block copolymers.

The fiber grade PET used in this study was kindly provided by the Akzo Corp. The material had a reported melting transition of 273°C and an inherent viscosity of 2.04 (dl/g). The PET was blended as received without further purification.

3.3 Experimental

3. 3. 1 Thermal Characterization

The transition temperatures of the liquid crystalline block copolymers were measured calorimetrically using a TA Instruments 2910 differential scanning calorimeter. Temperature calibration was performed using an indium standard. Samples of approximately 10 mg were initially heated in a nitrogen atmosphere from 30 to 300°C at a heating rate of 20°C/min, followed by quenching with liquid nitrogen. Samples were then reheated to 350°C at a heating rate of 20°C/min. The reported transitions are the maximum peak temperatures observed during the second heating run.

The degradation temperatures in air were also measured using a TA Instruments 2950 thermogravimetric analyzer. Samples were scanned from room temperature to 600°C at a heating rate of 20°C/min. The reported degradation temperature corresponds to 0.5 % weight loss.

3.3.2 Fiber Formation

Powders of the thermotropic polyesters and PET were tumble mixed for 24 hr's. The amounts of block copolymer used in the blends were 5, 10, and 20 % by weight. The mixed polymer powders were then compression molded using a Carver laboratory press at 270°C for 1 minute. The compressed sample was consequently ground in an analytical mill to a particle size less than 1000 microns and dried at 120°C for a minimum of 24 hours. Compression molding followed by grinding was convenient for obtaining particles that effectively fed into the mini-extruder.

Once thoroughly dried, the blends were extruded and spun into fibers. Extrusion was carried out with a ¼ inch Randcastle single screw mini-extruder. The mini-extruder

has four temperature zones which may be varied independently. The feeding, compression and melting sections, zones one, two and three respectively, were set at 220°C, 260°C and 280°C. The temperature of the die zone was varied to observe the effects on fiber spinning. The main criteria for determining the die temperature was the ability to obtain a uniform melt without die swell. The screw speed was held constant at 30 rpm corresponding to a flow rate of 1.5 g/min and a polymer residence time of two to four minutes within the extruder. The residence time in the extruder was kept to a minimum in order to reduce the possibility of transesterification reaction between the blend components.

Upon exiting the die of the extruder, the polymer was stretched using a custom built take-up device. A take up speed of 75 m/min. was used for all systems which corresponds to an approximate stretch ratio of 300 to 400. The stretch ratio for each system was determined as the ratio between the die and the drawn extrudate cross-sections (A_0/A_f). The round hole capillary die had a diameter of 1575 μm and an aspect ratio of ten. Fiber diameters were determined by optical microscopy.

The heat treatment of poly(ethylene terephthalate) fibers is an important processing stage that determines the ultimate properties of the material. A two step post-treatment process was performed immediately following the spinning process. Post drawing was accomplished using a continuous process between optoelectronically monitored feed and take-up spools. Cold drawing was performed at 85°C using a standard laboratory hot plate. The speed of the feed spool was kept constant at 4 m/min while the speed of the take-up winder was continuously monitored and increased until a stable neck was observed. For neat PET this occurred at a draw ratio of 3.5.

Hot drawing was accomplished using a similar procedure at a temperature of 205°C. The maximum draw ratio was determined by slowly increasing the speed of the take-up spool until excessive filament breakage occurred. The speed of the take-up spool was then decreased until drawing could proceed for at least two minutes without filament

breakage. For neat PET this corresponded to a maximum hot draw ratio of 1.5 and a total fiber draw ratio of 5. The total draw ratio was calculated as the ratio of the as-spun and final post treated fiber cross sections. All samples were collected and tested at the maximum draw ratio unless otherwise specified.

3.3.3 Tensile Testing

Tensile tests were performed on an Instron 1113 tensile tester connected to a personal computer. In order to facilitate mounting and alignment specimens were mounted onto paper tabs. Fiber diameters were measured using an Olympus microscope equipped with a calibrated scale accurate to $\pm$ 0.5 microns. A minimum of five diameter measurements per fiber were obtained. The applied strain rate was 10 percent elongation per minute, with an initial gage length of 50 mm. A 550g Toyo TI550 load cell measured the fiber load. The Young's modulus was determined from the best linear fit through the initial region of the stress-strain curve. Some typical stress-strain curves are shown in the appendix. Instrument compliance was measured and the apparent modulus was found to be approximately 2 percent lower than the true modulus. Samples that exhibited grip failure were omitted from the tenacity and ultimate elongation results. Each tensile property was averaged over nine tests and performed at ambient conditions in the laboratory. Standard deviations ranged from 5 to 10 percent for each system.

3.3.4 Thermal Instability

Shrinkage experiments were performed by placing the fibers in a convection oven preheated to 190°C for 15 minutes. Prior to heating, the fibers were conditioned for 24 hours at 21°C and 68 % relative humidity. The sample lengths before and after heating were determined at ambient temperature by straightening the fibers with a small load and

measuring the initial (L_0) or final (L_1) length respectively. All samples were approximately 20 cm in length before testing. After removal from the oven, the fibers were reconditioned for one hour and the resultant dimensional changes determined. The free shrinkage was computed as

$$\text{Shrinkage [\%]} = (L_0 - L_1)/L_1 * 100.$$

Shrinkage values were averaged over 5 measurements.

To measure the development of shrinkage stresses, force-temperature experiments were carried out using a TA Instruments 2940 thermal mechanical analyzer. This technique applies a constant strain and measures the development of thermal stresses with temperature change. The fibers were placed in the TMA and an initial strain of 0.05% imposed on the samples. The temperature was then increased at 5°C/min to 190°C and the resultant load monitored. After being held at 190°C for 15 min, the fiber was slowly cooled to room temperature and the shrinkage stresses at 190° and 30°C recorded.

3.3.5 Morphology

The morphology of the blends was investigated by optical microscopy (OM) and scanning electron microscopy (SEM). Fiber cross sections were prepared by mounting the samples in an epoxy matrix and fracturing the sample after cooling in liquid nitrogen. Fibers were also etched with a 60 parachlorophenol / 40 tetrachloroethane mixture to remove the PET. The solvent mixture was slowly dropped onto the fibers at 5 ml per minute for approximately 1 minute. All SEM samples were mounted on aluminum stubs, sputtered with gold using an SPE Sputter Coater, and characterized using a JEOL [JSM-35C] scanning electron microscope. An accelerating voltage of 20 kv was used. An Olympus microscope equipped with a Linkam hot stage was used for observing the blends before and after processing.

3.4 Results and Discussion

3.4.1 Thermal Behavior

The results of DSC and TGA scans for the four different block copolymers containing the Triad4 mesogen are presented in Table 3.1. Variables that were investigated included wt. % rod content, PBT block size and rod block size. To determine the wt. % rod content incorporated into each block copolymer, the rigid portions of the Triad and Diad sequences were accounted for but not the methylene flexible spacers.

Table 3.1. Thermal Characteristic of the various block copolymers.

	T_m1 (°C)	T_m2 (°C)	T_d (°C)	Wt. % Mesogen
Triad4 (2:4:21)	214	279	291	30
Triad4 (2:4:7)	202	282	302	49
Triad4 (2:4:3)	197	282	315	66
Triad4 (2:6:7)	205	281	336	55
Triad2 (2:4:7)	195		328	51
Triad2 (2:6:7)	193		336	57

These block copolymers exhibit two melting transitions and a complex phase behavior. The initial transition point (T_m1) corresponds to the melting of PBT blocks and diad moieties. The diad moieties are mesogenic and optical microscopy reveals that after this transition the polymers are biphasic exhibiting both nematic and isotropic characteristics. See figure 3.3. The second transition (T_m2) corresponds to the diad moieties becoming isotropic and the melting of the Triad mesogenic units [15]. For all of the Triad4 systems this transition occurred around 281°C. The temperature of this transition was independent of the mesogen content in the system.

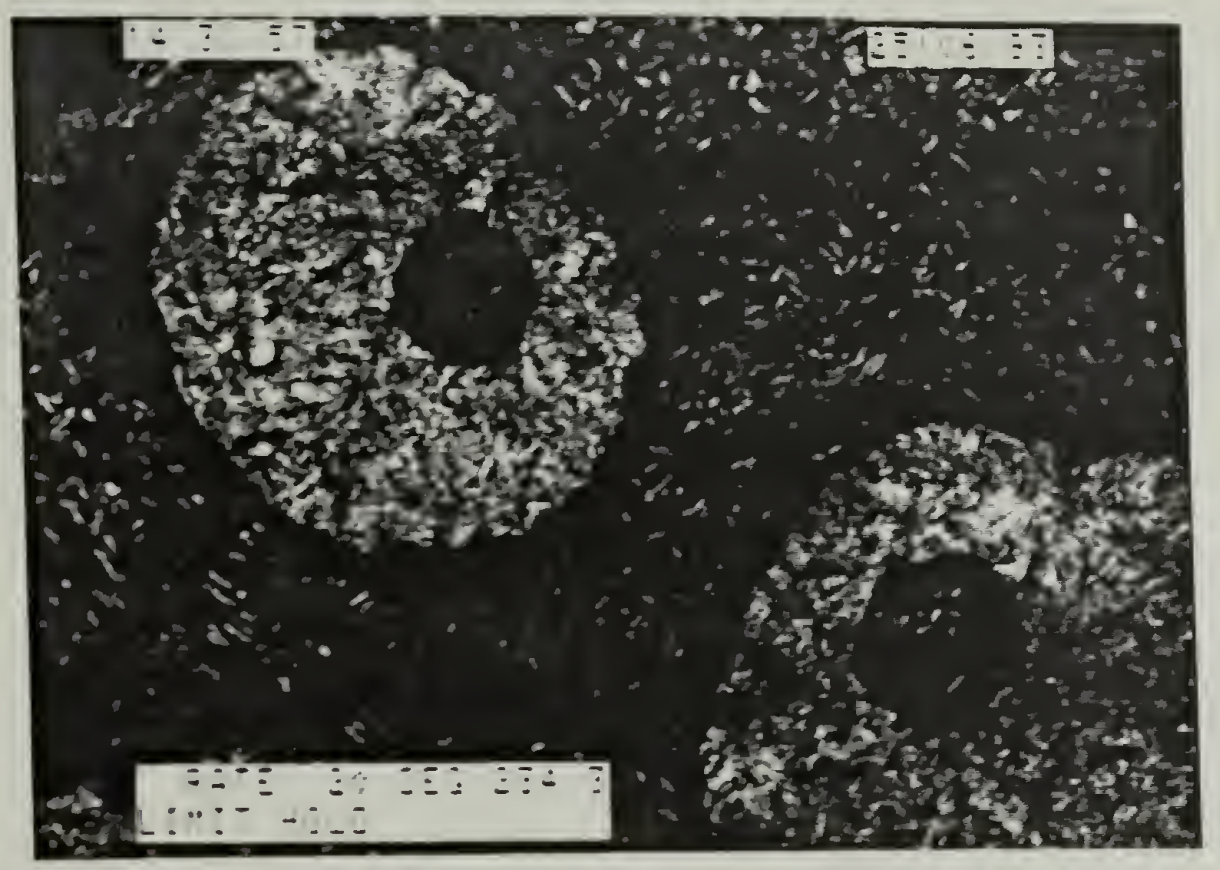


Figure 3.3. Optical micrograph of the Triad4 (2:4:7) block copolymer melt above the initial transition point (T_m1). Observed with crossed polarizers and magnified of 200 times.

The first transition temperature (T_m1) corresponds very well with the amount of PBT incorporated into the polymer. Triad4 (2:4:21) had the largest PBT blocks and the highest initial transition temperature at 214°C. Decreasing the block size to 7 units in the Triad4 (2:4:7) and Triad4 (2:6:7) systems dropped the initial transition point to 202 and 205°C respectively. Shortening the PBT block size to 3 units in the Triad4 (2:4:3) polymer further decreased the first transition to 197°C. This trend was not unexpected since longer PBT segment should permit the formation of crystallites with fewer defects and thus a higher melting temperature. Decreasing the length of PBT segments increases the number of defects in the crystallite structure and lowers the transition temperature. This trend may continue until a critical length is reached whereupon crystallization is no longer possible or melting is undetectable by DSC.

The degradation temperature (T_d) of these polymers, as determined by TGA, was dependent upon the amount of PBT in the system and the size of the mesogenic block.

As the amount of PBT in the polymers was decreased the decomposition temperature increased from 291°C for the 2:4:21 system to 315°C for the 2:4:3 polymer. However the variable having the greatest impact on the degradation temperature was the mesogenic block length. Increasing the Triad block length from 4 to 6 units increased the degradation temperature of the polymer from 302°C to 336°C. The reason for this increase is not yet understood since it cannot be attributed solely to the amount of rigid rod in the block copolymers. For instance, the Triad4 (2:4:3) polymer has approximately 10 % greater rod content than the Triad4 (2:6:7) polymer but the degradation temperature was 21°C lower.

The Triad2 systems have different transition temperatures when compared to the Triad4 systems, but the trends are similar. The two Triad2 systems investigated have identical PBT block sizes, 7 units, and initial transition temperatures that are very close i.e. 195°C and 193°C respectively. Furthermore, increasing the size of the mesogenic block from 4 to 6 units increased the degradation temperature from 328°C to 336°C. A second transition temperature was not detectable for these systems. Thus the Triad2 segments may be amorphous or the melting point of Triad2 crystals is above the degradation temperature of the polymer. The latter explanation is more plausible since a glass transition temperature was not readily apparent for these copolymers and the Triad2 homopolymer is known to melt at 360°C [16]. Observation of these polymers with an optical microscope equipped with a hot stage reveals that these polymers were fluid and exhibited a biphasic morphology above the first transition temperature similar to the Triad4 copolymers.

3.4.2 Triad4 Mechanical Performance

The mechanical properties for the hot drawn 20% Triad4/PET blends are shown in Figure 3.4. It is evident from the tensile data that varying the size of the PBT block has

very little effect on the final fiber properties. The Triad4 systems having mesogen block lengths of 4 units all have moduli similar to the PET control although the Triad4 (2:4:7) system does exhibit a small increase to 20 GPa. The largest increase in modulus, 21 GPa, was seen when the mesogen block size was increased from 4 to 6 units. This result was unexpected, it was thought that the absolute rod content of the block copolymers would be the controlling variable for achieving improvements in fiber modulus. However, the length of the mesogenic block appears to have a greater impact on the final fiber stiffness indicating a critical mesogenic block length may be necessary to attain maximum reinforcement of the PET matrix.

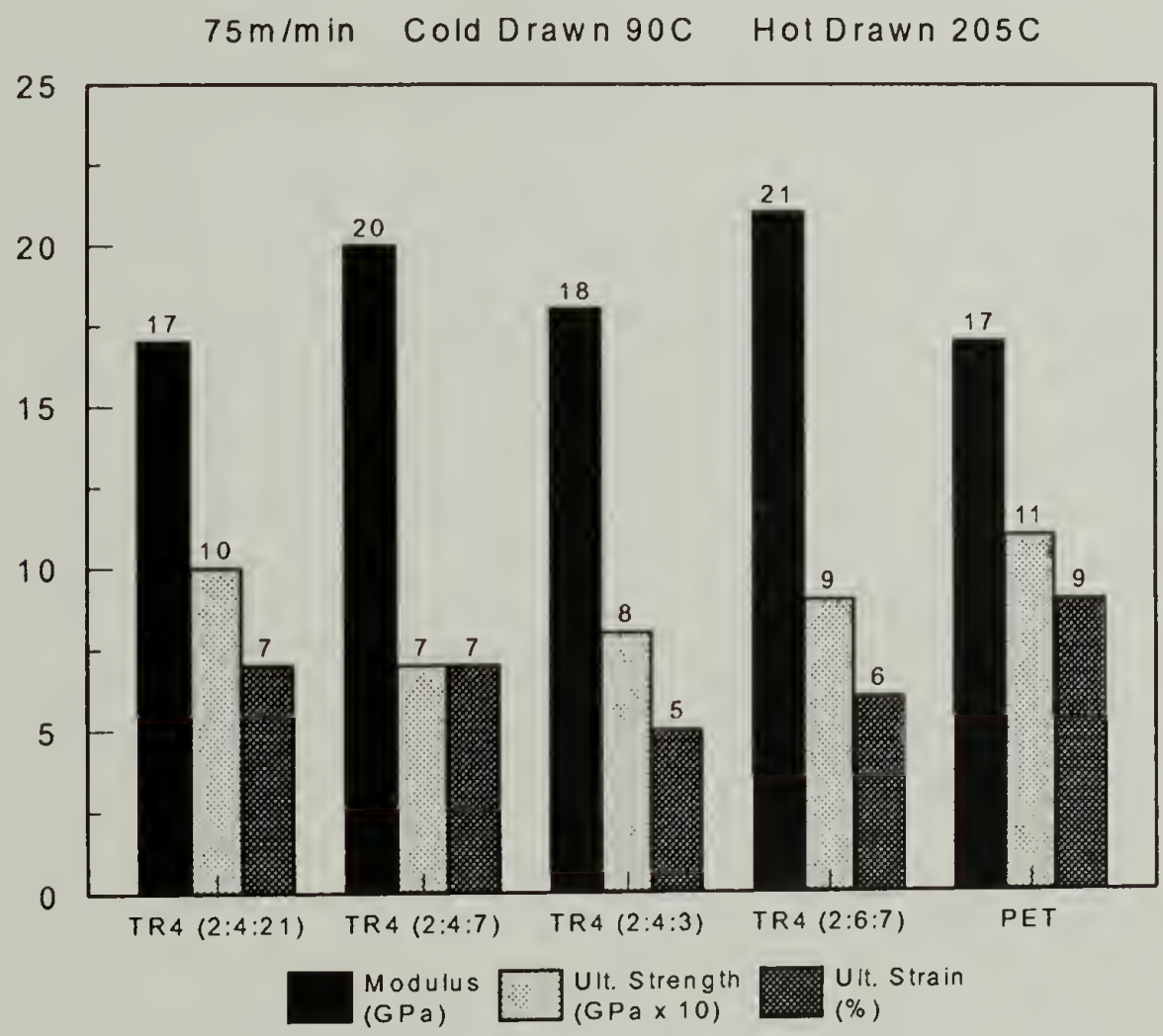


Figure 3.4. Tensile performance of the hot drawn 20% Triad4/PET blends.

The ultimate strength and strain to break are slightly lower for the blends when compared to the PET control. However these properties are not considered crucial when

evaluating these materials as potential reinforcing agents for PET. The ultimate strength and strain to break may be influenced by many factors such as the number of fiber defects and the molecular weight of the TLCP's. These variables are difficult to optimize when screening many different systems with very small quantities of material. Thus the major criterion for determining a systems effectiveness at this juncture is the fiber modulus since this quantity is less sensitive to processing variables.

To determine the effect of TLCP concentration on the moduli of the fibers, blends of 5, 10 and 20 wt. % LCP were evaluated. The results are shown in Figure 3.5.

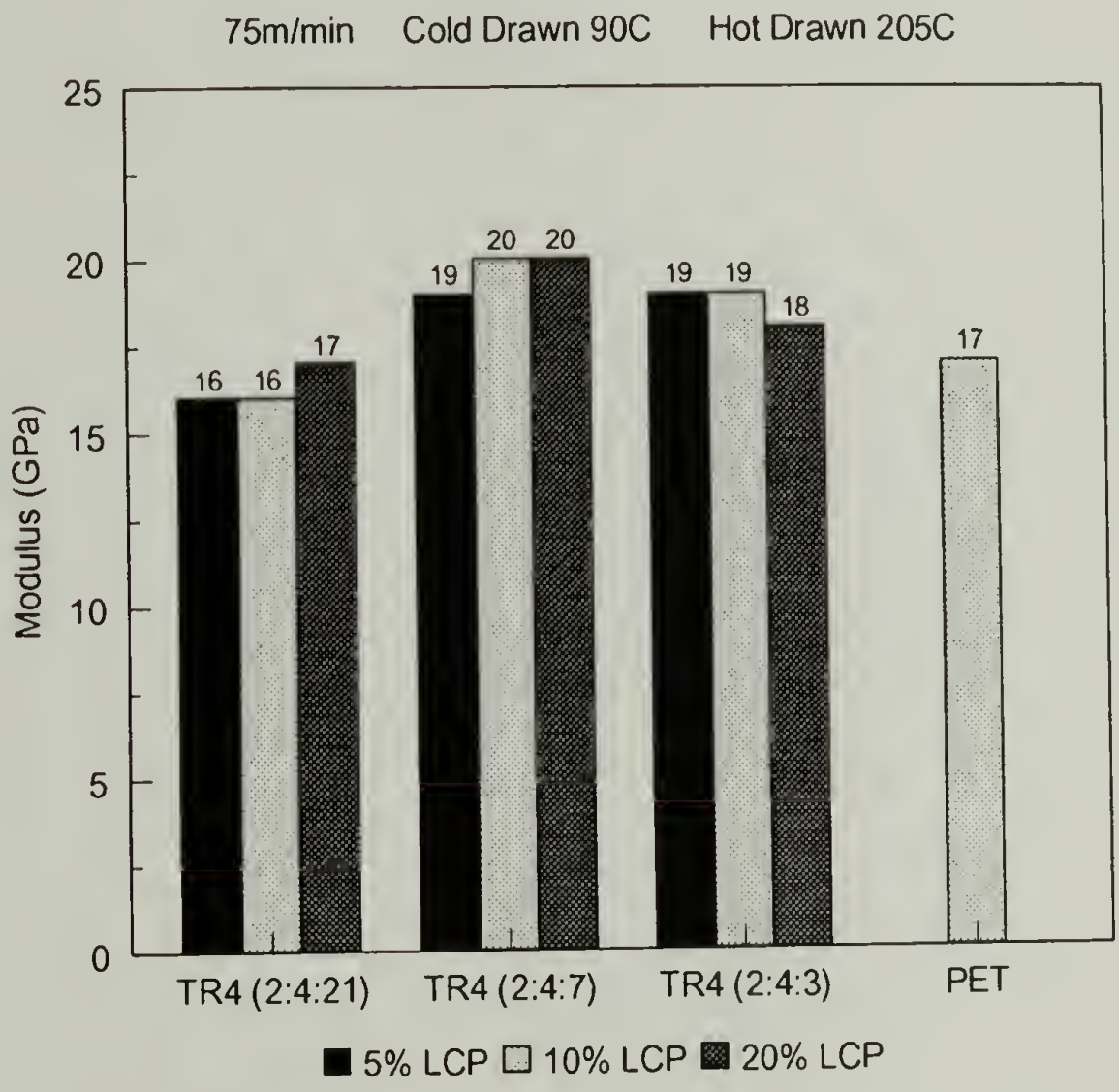


Figure 3.5. Fiber moduli versus wt. % Triad4 content.

Surprisingly increasing the percentage of rigid rod incorporated into the fiber did not appear to have a significant effect on the modulus. The 5 and 10 wt. % blends have

almost identical properties to the 20% blends. Thus the moduli appear to be independent of the LCP loading level and very consistent for each system. Essentially, low loading levels of the Triad4 (2:4:7) LCP are just as effective at obtaining small improvements in the fiber modulus as higher loading levels. Loading levels lower than 5 wt. % have not yet been evaluated to determine the extent of this phenomena. A trend based on the amount of rod in the system or the length of the PBT unit could not be found. However, the modulus of the Triad4 (2:4:21) system was slightly lower than either the Triad4 (2:4:7) or the Triad4 (2:4:3) systems suggesting large flexible blocks may reduce the ability of the block copolymers to improve or maintain fiber performance.

3.4.3 Triad4 Dimensional Instability

The free shrinkage of the 20% Triad4/PET blends is shown in figure 3.6. Two clear trends are visible based on the amount of PBT in the block copolymers and the length of the mesogenic segment. As the amount of PBT is increased in the block copolymers the dimensional stability of the fibers is decreased significantly from 10 % free shrinkage, for the Triad4 (2:4:3) system to 14 % for the Triad4 (2:4:21) system. Thus a high rod content improves the thermal stability of the blends, but comparison to the PET control reveals no overall improvement in fiber performance. However, further improvement in dimensional stability could be obtained by increasing the mesogenic block length from 4 to 6 units. The Triad4 (2:6:7) system, which exhibited only 8% free shrinkage, was the only Triad4 blend to exhibit increased dimensional stability compared to the PET control. Thus increasing the mesogen block length improved both the mechanical and thermal behavior of the fiber compared to the PET control while increasing the absolute rod content only resulted in minor performance improvements at best.

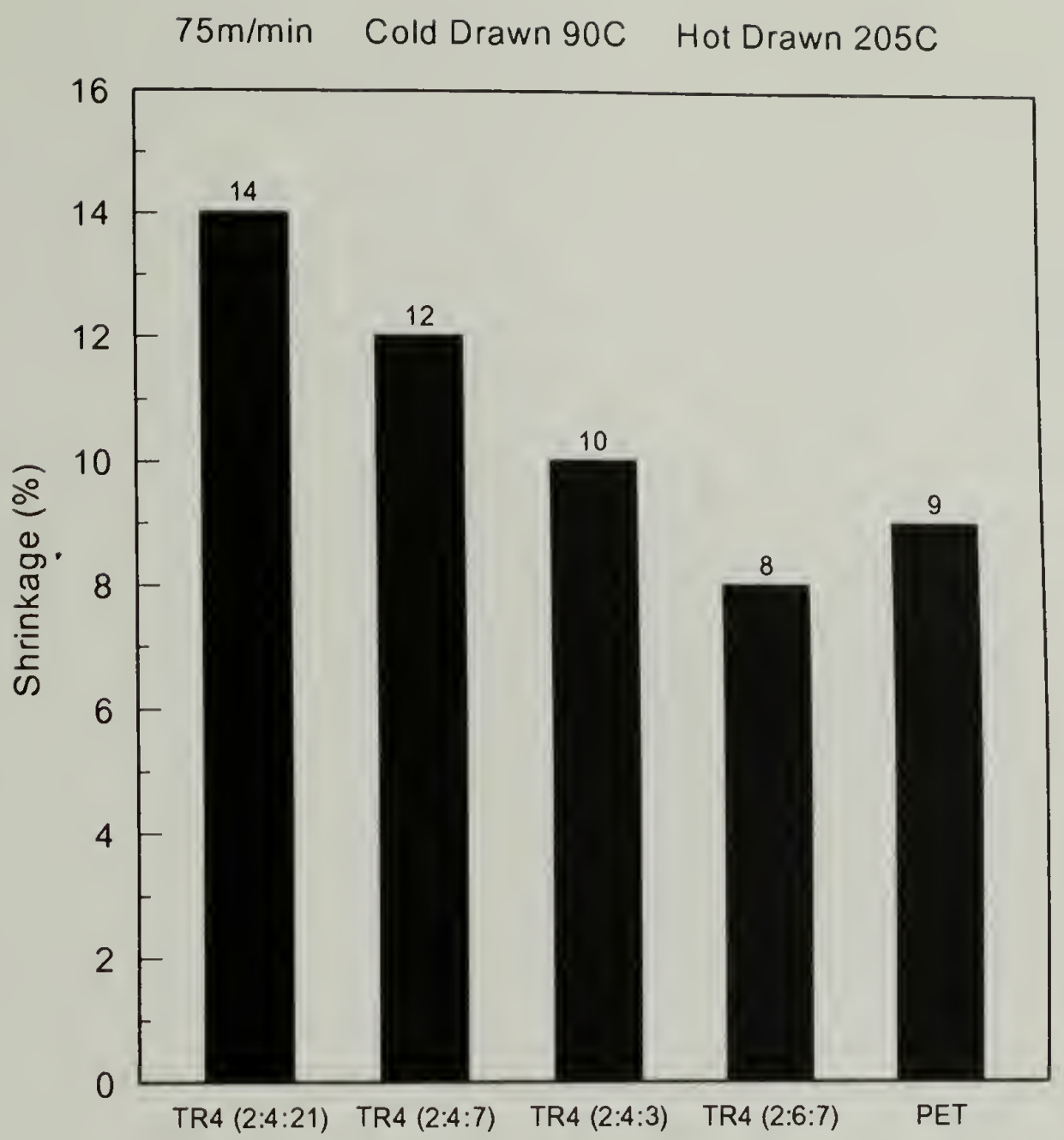


Figure 3.6. Free shrinkage of the 20 % Triad4/PET blends.

3.4.4 Triad4 Morphology

A fiber cross section of the as-spun 20% Triad4 (2:4:7) blend is shown in figure 3.7. The sample was fractured after cooling with liquid nitrogen and studied using Scanning Electron Microscopy (SEM). Observation of the fracture at a magnification of 20×10^3 revealed a particulate morphology with sub-micron particles that ranged in size from 0.05 to 0.3 microns. The block copolymer was evenly distributed throughout the fiber cross section and no evidence of a skin-core morphology could be detected. The numerous indentations visible on the surface can be interpreted as imprints of missing LCP particles

removed during sample preparation. Evidence of adhesion between the phases was also absent although the two materials are chemically similar and some interaction between components was expected. Shin and Chung [17, 18] reported excellent adhesion between PET and a thermotropic liquid crystalline polyester when flexible moieties were incorporated into the LCP reinforcement material. Examination of fiber cross sections for other 20% Triad4 blend systems revealed similar morphologies and characteristics to the Triad4 (2:4:7) system. The geometry of the block copolymer could only be determined in the as-spun fiber specimens i.e. the block copolymers phase could not be identified in the post-treated fibers using SEM. Due to the high degree of crystallinity in the drawn fibers and the chemical similarities between the two blend components, attempts to distinguish between the phases by solvent etching were not successful.

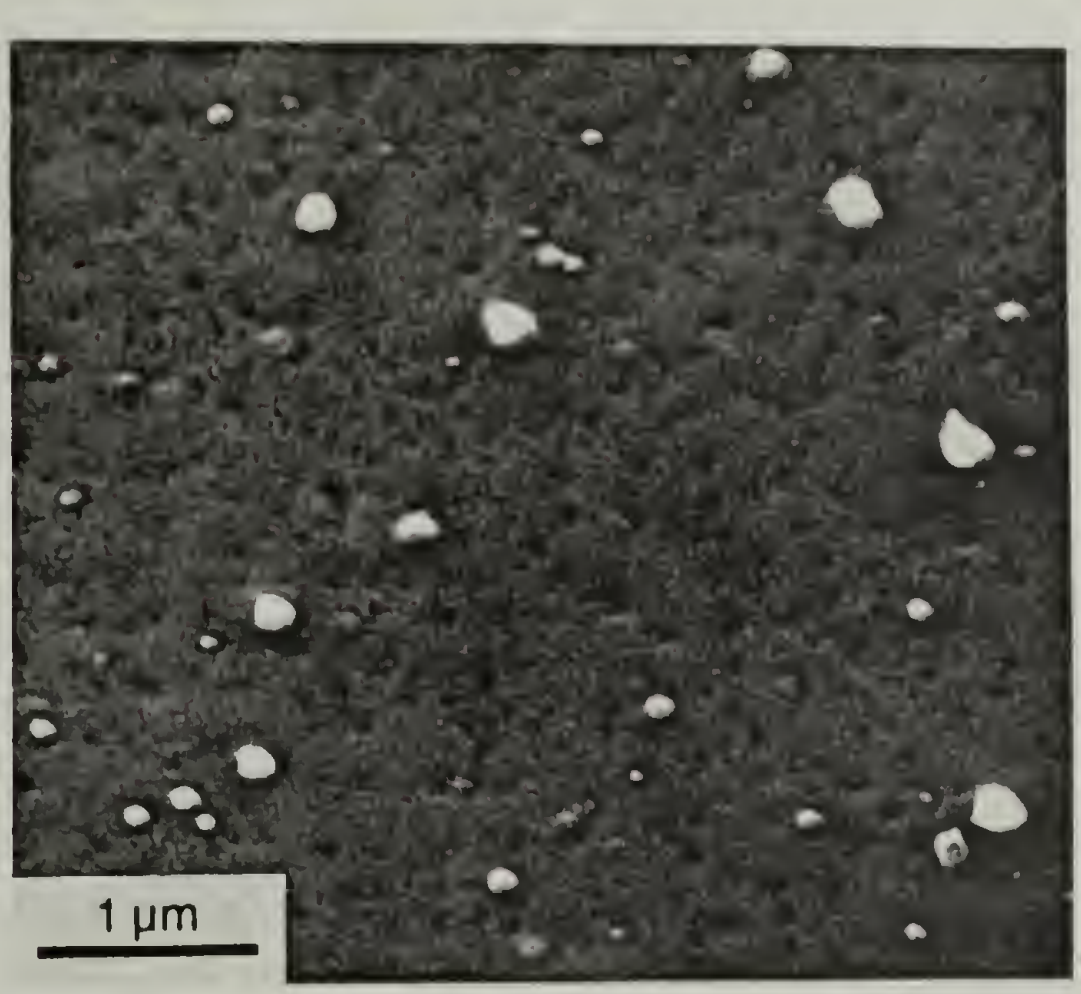


Figure 3.7. Fiber cross-section of the as-spun 20% Triad4 (2:4:7) blend. The sample was cryogenically fractured after cooling with liquid nitrogen and magnified 20, 000 times using SEM.

The small increase in tensile performance for the Triad4 systems is surprising when the lack of LCP orientation and fibrillation is taken into account. It is generally observed that fibrillation of the LCP phase is necessary for good reinforcement of the PET matrix material [19-22]. Fibril formation in LCP-polymer blends depends on many factors such as composition, processing conditions, viscosity ratio of the component polymers, and the rheological characteristic of the matrix polymer [7]. Since only small quantities of the block copolymer materials were available, the processing conditions could not be optimized for these systems.

3.4.5 Triad2

A slightly stiffer class of block copolymers have also been evaluated for their ability to reinforce PET fibers. These systems are based on the Triad2 mesogenic unit. The Triad2 copolymers are very similar to the Triad4 systems except two methylene groups have been removed from the mesogen. This should reduce the amount of flexibility incorporated into the mesogenic unit.

3.4.5.1 Triad2 Mechanical Performance

A comparison of post-treated 20% Triad/PET fiber blends is shown in figure 3.8. Both of the Triad2 systems investigated dramatically increased the moduli of the fibers compared to the PET control. The largest increase was seen for the Triad2 (2:6:7) system which attained a modulus value of 24 GPa. This is a 40% increase over neat PET. Furthermore a trend that was apparent in the Triad4 systems was also visible in the Triad2 blends i.e. increasing the length of the mesogenic unit from 4 to 6 units appears to increase the effectiveness of the Triad2 as a reinforcing agent. Increasing the length of the mesogenic block from 4 to 6 units in the Triad4 system increased performance from 20 to

21 GPa respectively, while increasing the block length for the Triad2 systems increased the modulus from 23 to 24 GPa. Although the increase was within experimental error for both the Triad4 and Triad2 systems, the trend is consistent. Comparing the Triad4 and Triad2 systems containing similar block sizes suggests that a 3 GPa increase in fiber moduli may be directly attributed to the increased stiffness of the Triad2 mesogenic unit.

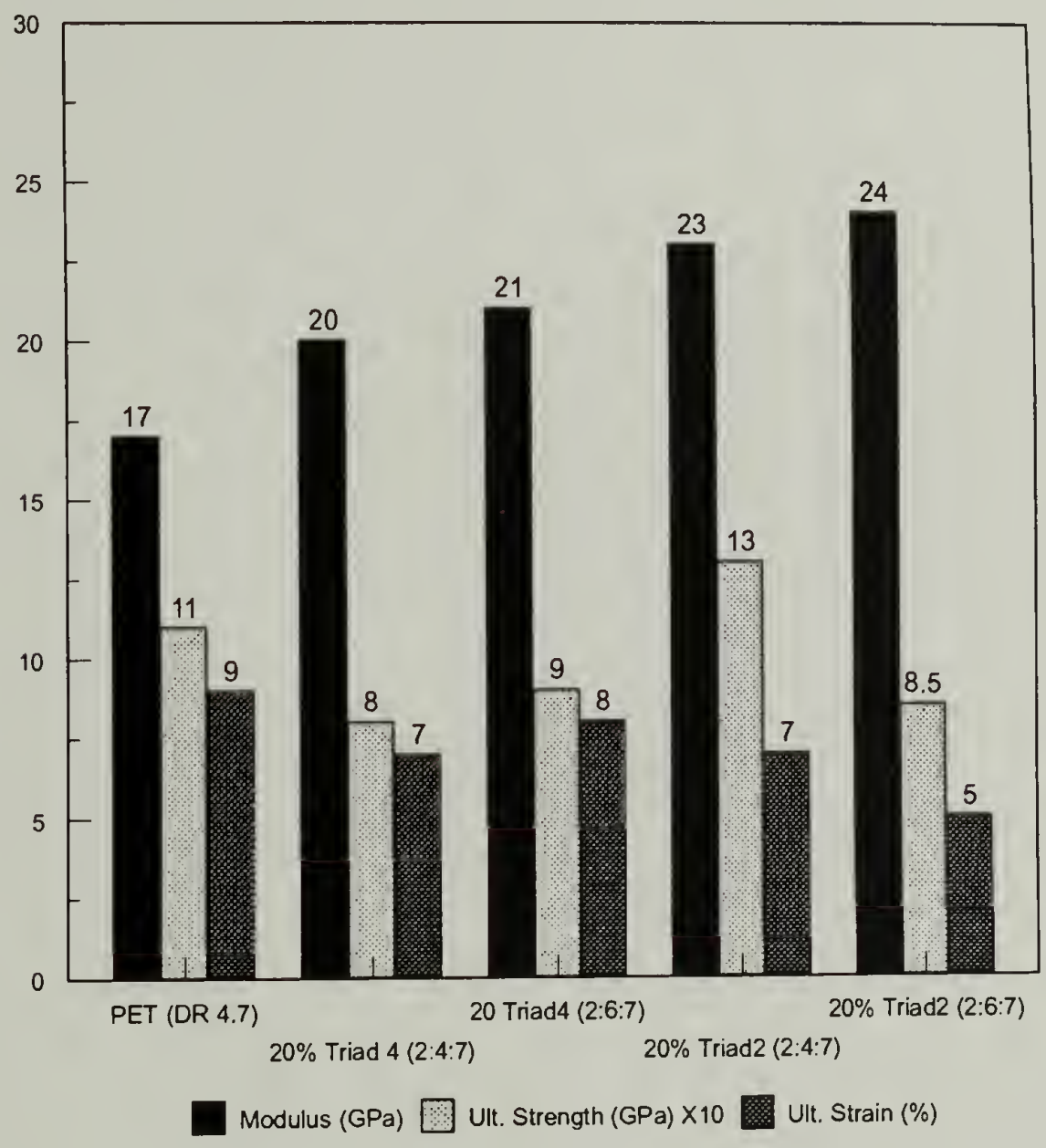


Figure 3.8. Comparison of the mechanical properties for the 20 % Triad4 and Triad2 blends.

As mentioned previously the ultimate strength and the strain to break of the blends are not considered to be determining factors at this juncture of the study. However it is interesting to point out that the Triad2 (2:4:7) system had a strength of 1300 MPa which

was 200 MPa greater than the PET control. This is important since it shows that the strength of the fibers can be improved and that the decrease in ultimate strength typically observed for these blends is not an inherent problem with these systems. Thus optimization of synthesis and processing may lead to significantly stiffer and stronger fibers compared to neat PET.

The properties of the Triad2 systems were very sensitive to processing temperatures as shown in figure 3.9.

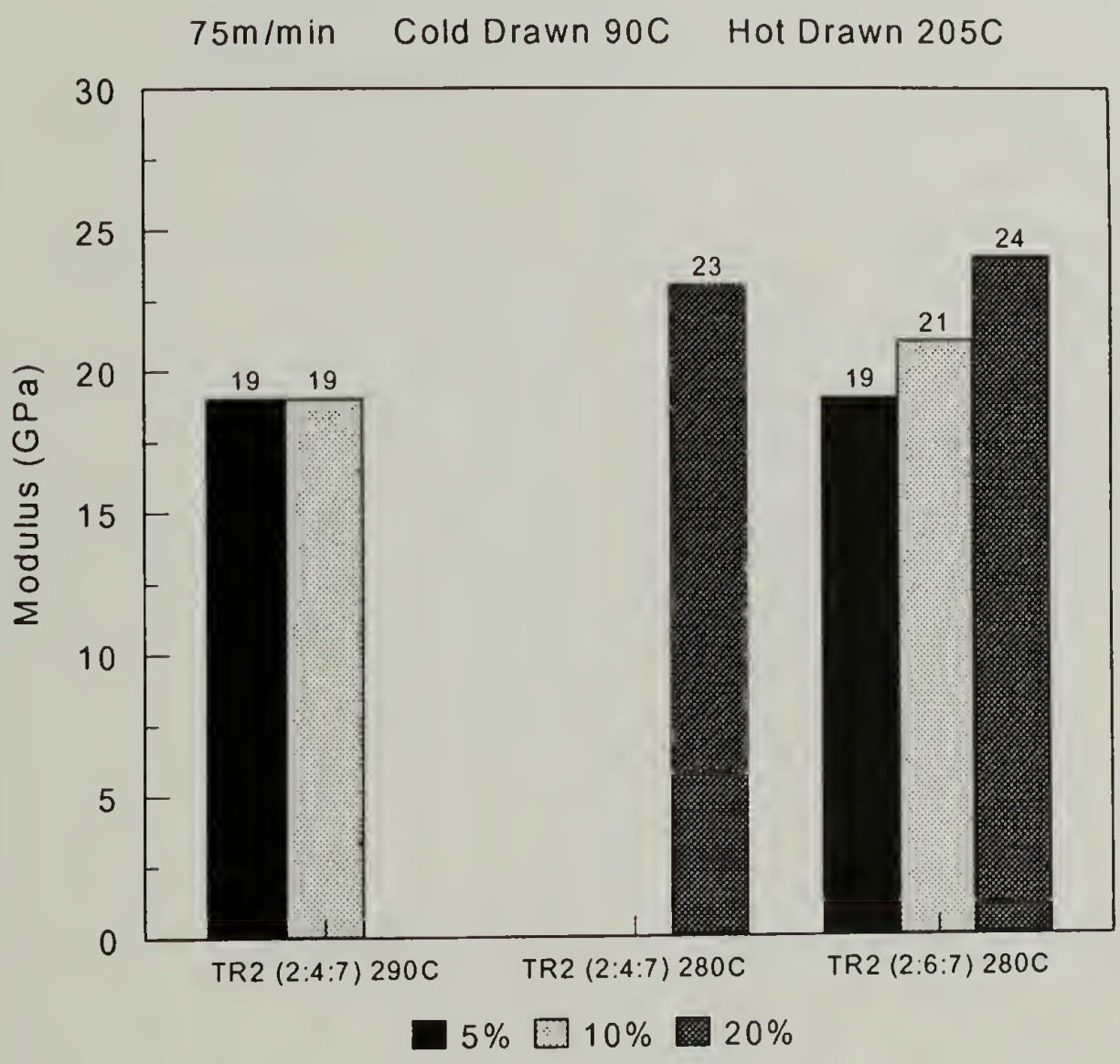


Figure 3.9. Properties versus processing for the Triad2 fiber blend systems.

Triad2 (2:4:6) blends were spun at 280 and 290°C. The 20 wt. % blend degraded at 290°C. Gas bubbles were clearly evident although the TGA indicated the system should have been stable to approximately 328°C. The 5 and 10 wt. % systems could be spun at

290°C without visible degradation in the spinning line but little or no improvement in properties could be detected. Degradation of the polymer may have been facilitated by exposure to high shear fields during extrusion. Thus thermogravimetric analysis may only be relied upon to give an upper bound to degradation when evaluating potential processing conditions. Decreasing the processing temperature to 280°C for the 20% Triad2 (2:4:7) blend eliminated any visible signs of degradation, improved fiber formation and lead to the large increase in fiber modulus. Due to limited amounts of material the 5 and 10 wt. % blends could not be spun at 280°C. The Triad2 (2:6:7) blends were all spun at 280°C. The 5 wt. % system showed only a minor increase in modulus to 19 GPa but the 10 and 20 wt % blends exhibited significant improvements of 21 and 24 GPa respectively. Thus there appears to be a definite increase in modulus with concentration which was the anticipated result. This result is contrary to the mechanical performance of the Triad4 systems which was independent of the block copolymer concentration. Other processing temperatures were not investigated for the Triad2 (2:6:7) system.

The effect of draw ratio was investigated for the 20% Triad2 (2:6:7)/PET blend. The results are shown in figure 3.10. As the draw ratio was increased from 4.5 to 5.5 the modulus increased from 18 to 24 GPa, the strength increased from 600 to 900 MPa and the strain to break decreased from 8 to 5 %. These tendencies are typical for drawn samples i.e. as the amount of orientation is increased in the fibers the mechanical properties are improved. The trend of increasing strength indicates that these fibers have not been overly drawn. The modulus of excessively drawn fibers may continue to increase slightly but there is a corresponding drop in fiber strength as tie molecules between crystallites are broken [23]. For these fibers a draw ratio beyond 5.5 was not feasible due to frequent fiber breakage in the drawing line. It is important to note that if higher draw ratios can be obtained through process optimization, strengths equivalent or superior to neat PET fibers may be achievable for this system.

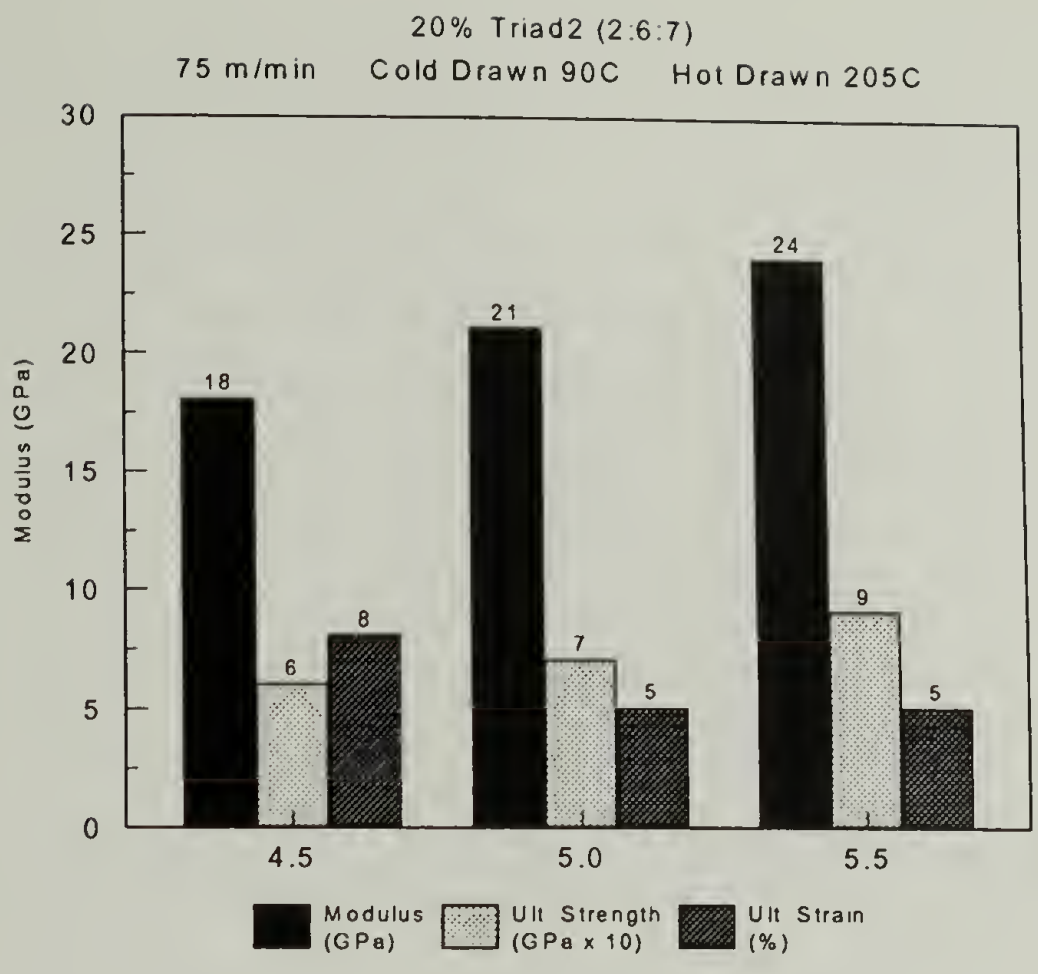


Figure 3.10. Modulus versus draw ratio for the 20 % Triad2 (2:6:7) system.

Due to limited quantities of the Triad2 (2:6:7) it has not been possible to determine the mechanical properties of the neat material, but the rule of mixtures can be used to estimate the modulus of the block copolymer. If it is assumed that PET constitutes 80 % of the fiber volume and contributes 17 GPa to the composite, a modulus of 52 GPa is obtained for the LCP phase. A stiffness of 52 GPa is in the regime of completely rigid polymers such as Vectra and implies that Triad2 (2:6:7) is indeed a high performance material. However all of the mechanical properties discussed so far have been for post-treated fibers, when the tensile properties for the as-spun fibers are examined no increase in tensile performance is observed. Figure 3.11 shows the moduli versus block copolymer content for the 5, 10 and 20 wt. % as-spun Triad2 (2:6:7) fiber blends. All of the as-spun blends exhibit a modulus equivalent to the PET control, 2 GPa, which contradicts the improvements obtained for the post-treated fibers. Thus the rule of mixtures does not

apply to the as-spun fibers and Triad2 (2:6:7) doesn't improve the tensile performance of PET fibers until after the post-treatment process. This is unusual behavior and suggests that the Triad2 (2:6:7) may actually be modifying the PET matrix rather than performing as a reinforcement agent. For instance if the block copolymer increases the orientation or the degree of crystallinity in the PET phase, an improvement in mechanical properties may be obtained. Another possibility is that the block copolymer phase may have been drawn and oriented during the post-treatment process. This is considered a possibility since the block copolymer is only semi-rigid and a considerable amount of flexibility has been incorporated into the polymer chain. Increasing the Triad2 (2:6:7) orientation via the drawing process may have improved the performance of the material to such an extent that mechanical reinforcement was possible.

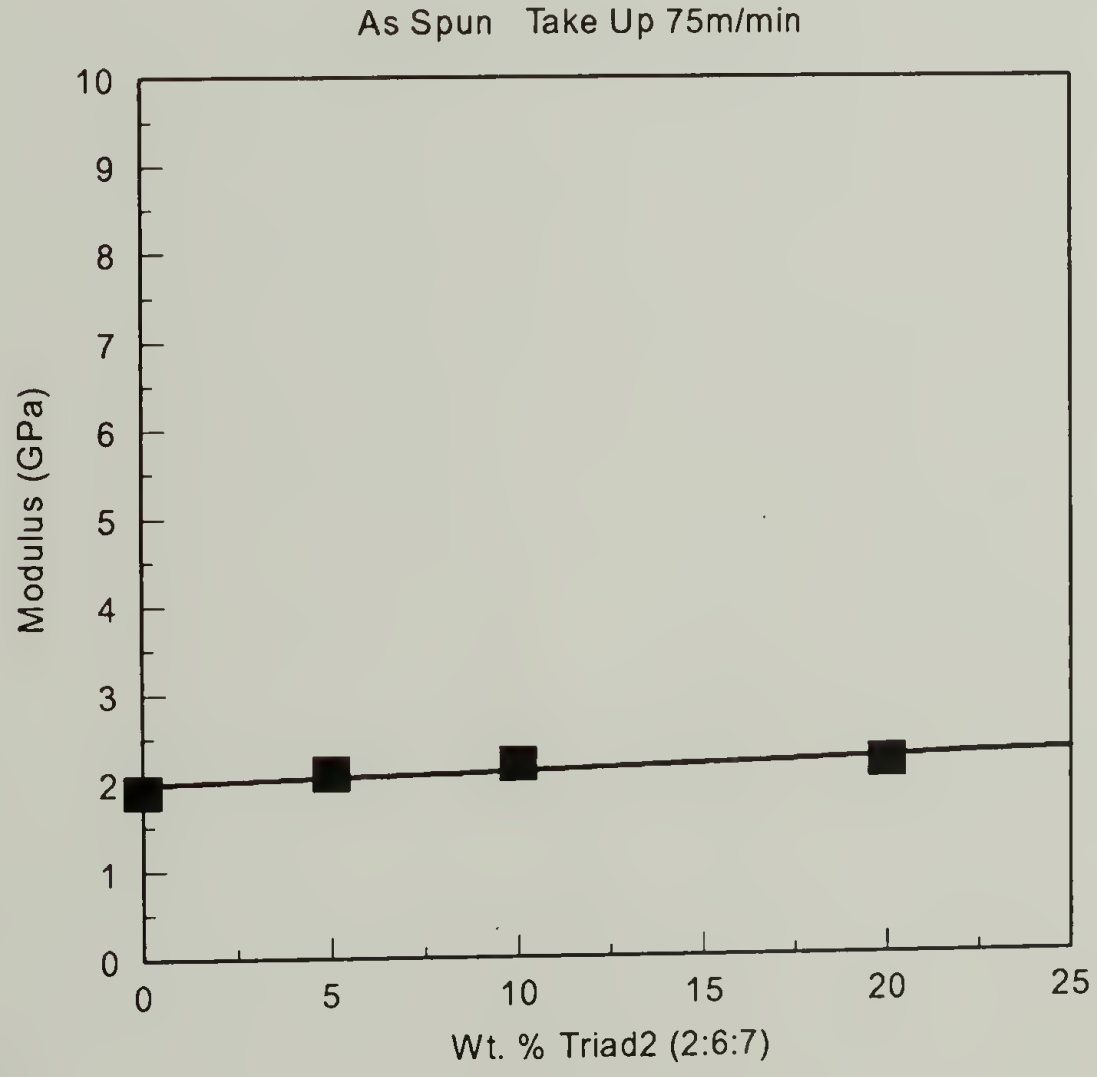


Figure 3.11. Modulus versus wt. % Triad2 (2:6:7) content for as-spun fibers.

3.4.5.2 Triad2 Dimensional Instability

PET fibers are often used in applications where thermal instabilities are undesirable. Fiber instabilities can cause dimensional changes which may ultimately result in the failure of a component. The degree of free shrinkage a fiber incurs at a particular temperature is typically reported as an indicator of it's thermal instability. The free shrinkage ($\sigma = 0$) is an important parameter to consider, particularly for applications where fibers are not under dimensional constraints i.e. clothing, carpets, etc. However for instances where the fibers are to function under dimensional constraints, such as composites, the development of shrinkage stresses must also be a primary concern. If the free shrinkage of the fiber is reduced but large shrinkage stresses develop upon heating, part warpage could still occur and ultimately result in failure of the composite. Similarly if fiber shrinkage remained constant but the stress was reduced, warpage might be avoided. Thus if the addition of a liquid crystalline polymer to PET could reduce fiber shrinkage and shrinkage stress it would be a major advantage for end use applications. An example of a PET fiber stress-temperature experiment is shown in figure 3.12. This technique applies a constant strain, typically 0.05 %, and measures the development of thermal stress with temperature change. For a uniaxially constrained sample this can be expressed as

$$d\sigma = -E\alpha dT$$

where σ = stress, E = tensile modulus, α = coefficient of thermal expansion, and T = temperature. Thus if the stress is measured as a function of temperature the slope will be the product of the modulus and thermal expansion coefficient.

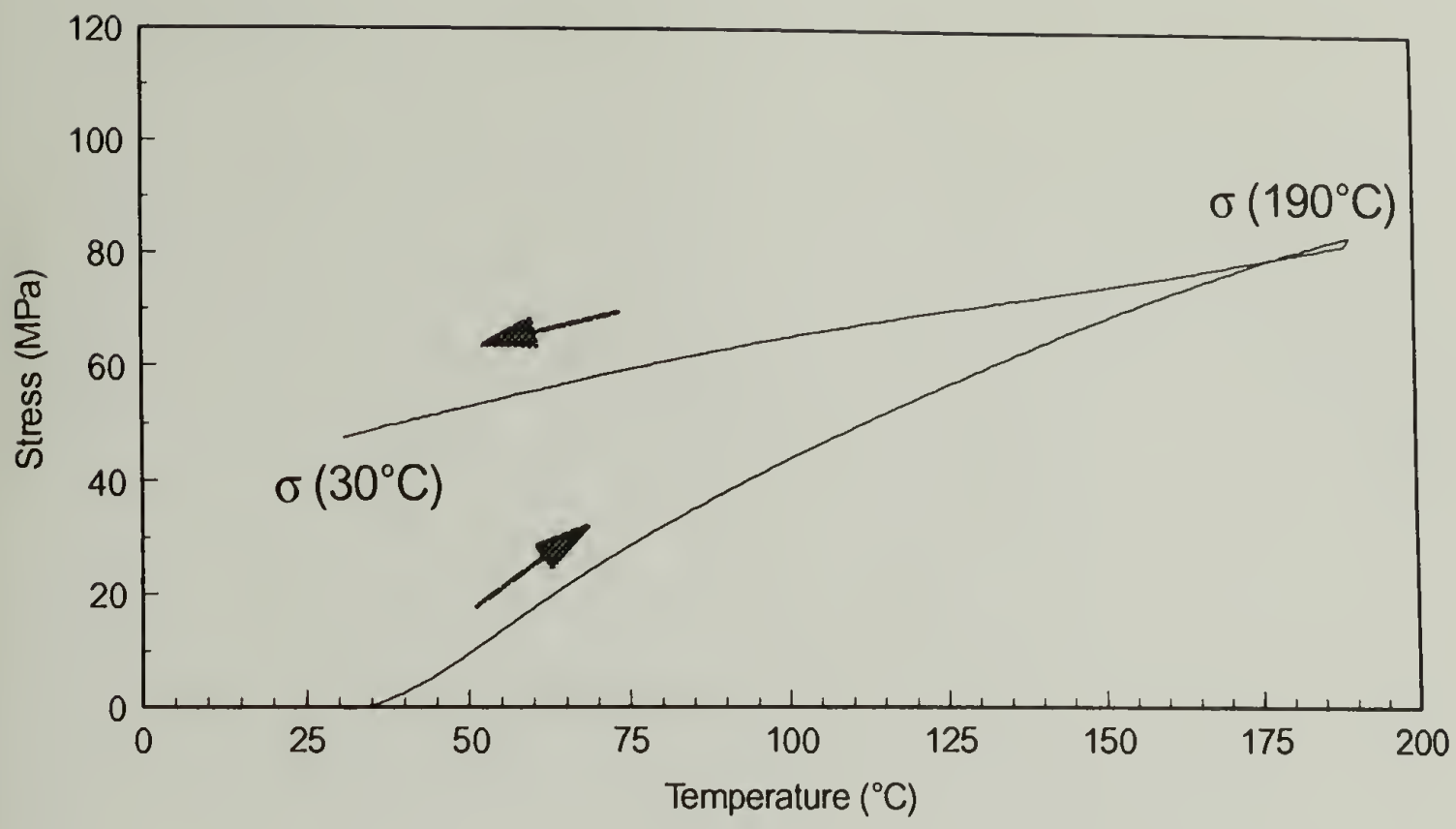


Figure 3.12. Stress versus temperature for the PET control fiber having a draw ratio of 5.0.

Table 3.2 reports the free shrinkage and stress-temperature data for the 20% Triad2 (2:6:7)/PET blend system at various draw ratios. Only the maximum shrinkage stress obtained at 190C and the residual stress at 30C have been reported. Furthermore the stress-temperature data have been normalized with respect to the initial load applied to the fiber. The PET control had a modulus of 17 GPa and an ultimate strength of 1100 MPa.

Table 3.2. Dimensional instability of the 20 % Triad2 (2:6:7) fiber blends as a function of draw ratio.

	Shrinkage Strain (%)	Shrinkage Stress (MPa)	
		30 °C	190 °C
PET Draw Ratio = 5.0	9	45	81
20 % Triad2 (2:6:7) Draw Ratio = 4.5	7	37	57
20 % Triad2 (2:6:7) Draw Ratio = 5.0	7	56	84
20 % Triad2 (2:6:7) Draw Ratio = 5.5	8	59	96

The addition of 20% Triad2 (2:6:7) to PET did reduce the free shrinkage of the fibers. Comparing fiber samples having a maximum shrinkage stress of approximately 80 MPa, the blended fiber exhibited 7 % free shrinkage while the PET control had 9 %. This is approximately a 30 % increase in fiber thermal stability at 190C. The Triad2 (2:6:7) also exhibited superior free shrinkage characteristics when compared to the 20 % Triad4 (2:6:7) system which had 8% free shrinkage. Thus the more rigid Triad2 mesogen appears to be more efficient at reducing dimensional instabilities and increasing the mechanical performance of PET fiber.

Although the free shrinkage was reduced in the blended fibers, applying draw ratios ranging from 4.5 to 5.5 increased the maximum shrinkage stress from 57 to 96 MPa. Thus the reduction in free shrinkage may only be considered a partial improvement in thermal stability since the fiber exhibiting superior tensile performance developed a higher peak shrinkage stress than the PET control.

Both the free shrinkage and the maximum shrinkage stresses in the 20% Triad2 (2:6:7) blend system were dependent upon the maximum draw ratio experienced by the fiber, a trend that was consistent with the PET control. This indicates that although the free shrinkage of the fibers has been reduced, the mechanisms responsible for dimensional instability in the fiber have not been significantly affected by the addition of the block copolymer. Long and Ward [24] suggested that the peak shrinkage force is due to the retraction of the shortest chains. It is these chains that are thought to control the load-bearing properties, particularly tensile modulus. Thus the higher stiffness, 24 GPa, found in the 20% Triad2 (2:6:7) system may be the result of a larger number of load-bearing chains in the fiber. This supports the hypothesis that Triad2 (2:6:7) may be modifying the PET matrix rather than mechanically contributing to the fiber performance as a true reinforcement material.

3.4.5.3 Triad2 Morphology

Cross-sections of 20% Triad2 (2:6:7) as-spun fibers, observed using scanning electron microscopy, revealed a distinct two-phase morphology. See figure 3.13. The LCP phase appears to be evenly distributed throughout the fiber cross-section with the exception of a 1 μm skin region rich in LCP content. See figure 3.14. Particle size varied and depended upon location within the fiber. Interior particles ranged from 0.5 to 2 μm in diameter while the particles located in the skin region appeared to have diameters in the range of 0.05 to 0.2 μm. The shape of the LCP phase also varied and appeared to consist of both particulate and elongated geometry's. Evidence of adhesion between the phases was not readily apparent but this could be an artifact of the sample preparation technique. For instance, it is well known that cracks tend to propagate along interfaces at liquid nitrogen temperatures. Furthermore thermal expansion differences between the components may also be a contributing factor.

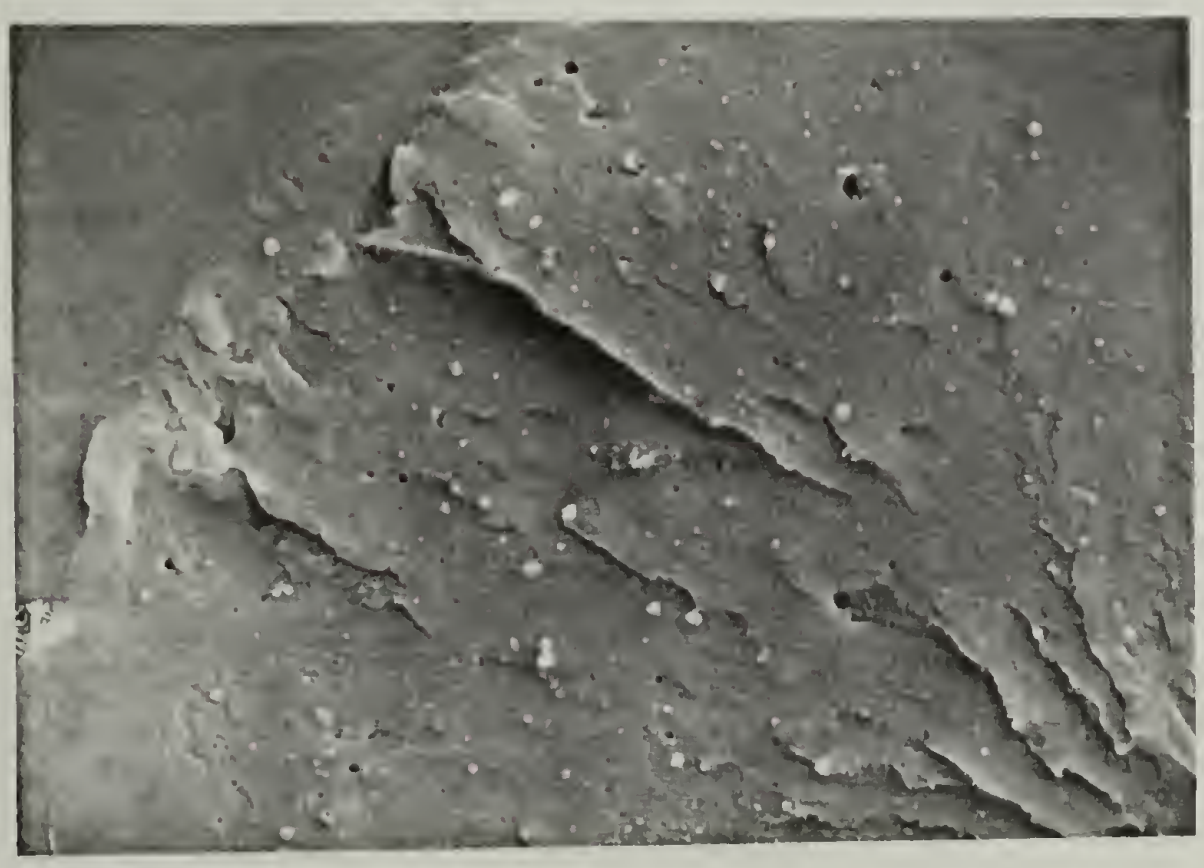


Figure 3.13. Fiber cross section of an as-spun 20 % Triad2 (2:6:7) blend fiber.

Figure 3.14. SEM evidence of a skin-core morphology present in the as-spun 20 % Triad2 (2:6:7) fiber.

Figure 3.15 is an optical micrograph of a solvent etched as-spun 20% Triad2 (2:6:7) fiber magnified 500 times. The fiber was etched using a 60/40 parachlorophenol tetrachloroethane mixture. LCP fibrils could be clearly seen in the fiber residue. The presence of a fibrillated Triad2 (2:6:7) phase indicates that the temperatures selected for processing were reasonable although they have not been optimized.

Scanning electron microscopy confirmed that at least some of the LCP phase was fibrillar and oriented along the fiber axis. See figure 3.16. The diameters of observed fibrils were approximately 1 to 2 μm and aspect ratios varied from 25 to 160. These aspect ratios are considerably smaller than those reported by other investigators and the number of fibrils was far less than would have been expected for an immiscible 20 wt. % blend [11, 25, 26]. Thus the Triad2 (2:6:7) may be partially miscible with the PET and/or the geometry of the LCP phase may have been predominately particulate.

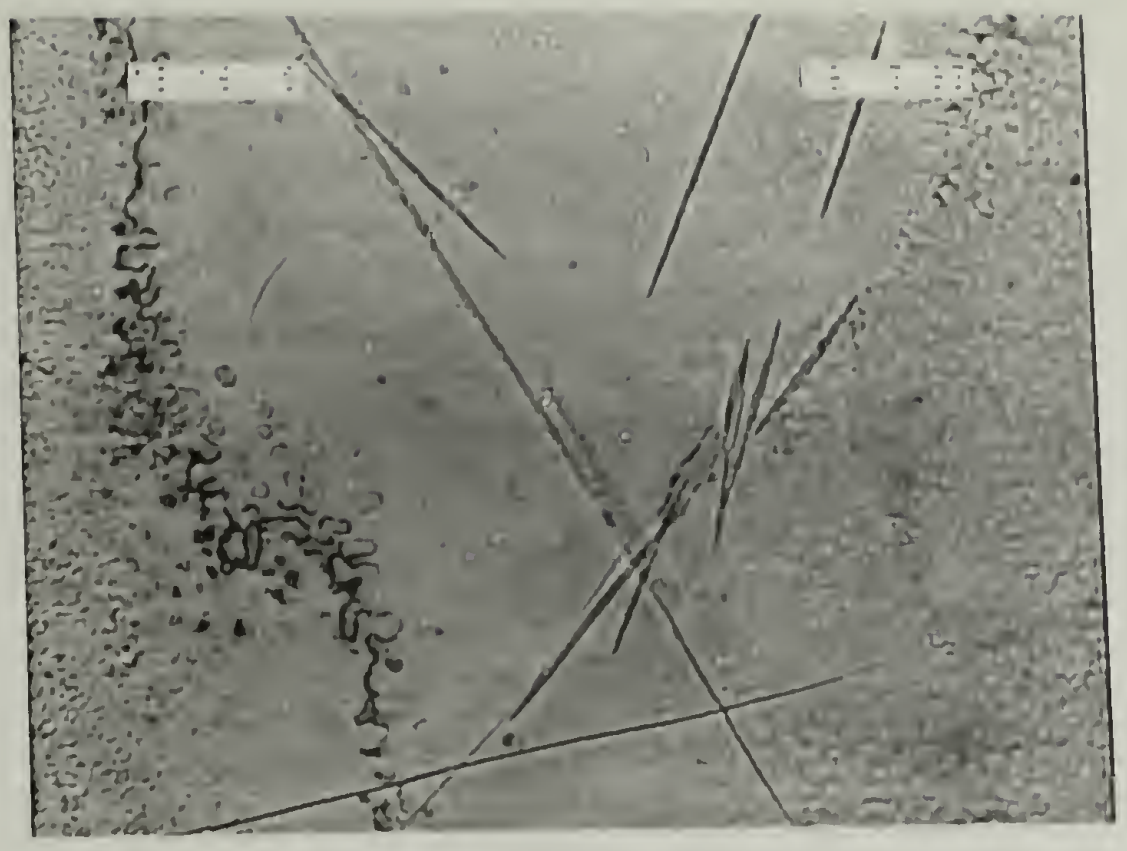


Figure 3.15. Optical microscopy evidence of fibril formation in the 20 % Triad2 (2:6:7) fiber after etching the PET matrix.

Figure 3.16. High magnification SEM micrograph of Triad2 (2:6:7) fibril after solvent etching the PET matrix.

Partial miscibility of the Triad2 (2:6:7) with the PET matrix can make fibril generation difficult, and a particulate morphology would not be readily visible with optical microscopy since it may have been susceptible to removal during the etching process [27]. Furthermore if the LCP particles were present but coated/covered with PET, scanning electron microscopy would be unable to distinguish between the two phases.

Comparison of the etched blend fiber with the etched PET control shown in figure 3.17 does reveal a dramatic difference in fiber morphology after etching. The PET fiber is smooth and etches evenly while the blend fiber has a very porous and rough surface structure. This difference in blend fiber structure may be due to particulates of the LCP phase being removed in an uneven fashion during the etching process. The Triad2 (2:6:7) may also be modifying the PET matrix slightly causing a change in the fiber's solubility. The extent of interaction between blend components is not yet known but partial miscibility or compatibility is considered a significant possibility particularly since a large portion of LCP cannot be accounted for at this point. Digital analysis of fiber cross sections indicates only 7 to 12 % block copolymer phase within the fiber, neglecting the 1μm skin region. Furthermore, examples of partial miscibility between thermotropic polyesters and PET are prevalent in the literature although the type and extent of interaction has not been adequately studied [10, 28-32].

The morphology of the as-spun fibers is further evidence that the Triad2 (2:6:7) polymer may not have remarkable properties. Although fibrillation of the Triad2 (2:6:7) phase was achieved, mechanical reinforcement of the PET was not observed. It is possible that the number of fibrils or their aspect ratios was insufficient to enhance the as-spun fibers but this is unlikely particularly at the 20 wt. % loading level. A more reasonable suggestion is that the inherent mechanical properties of the Triad2 (2:6:7) are poor. Thus the block copolymer phase cannot mechanically contribute to the improvement of the PET matrix.

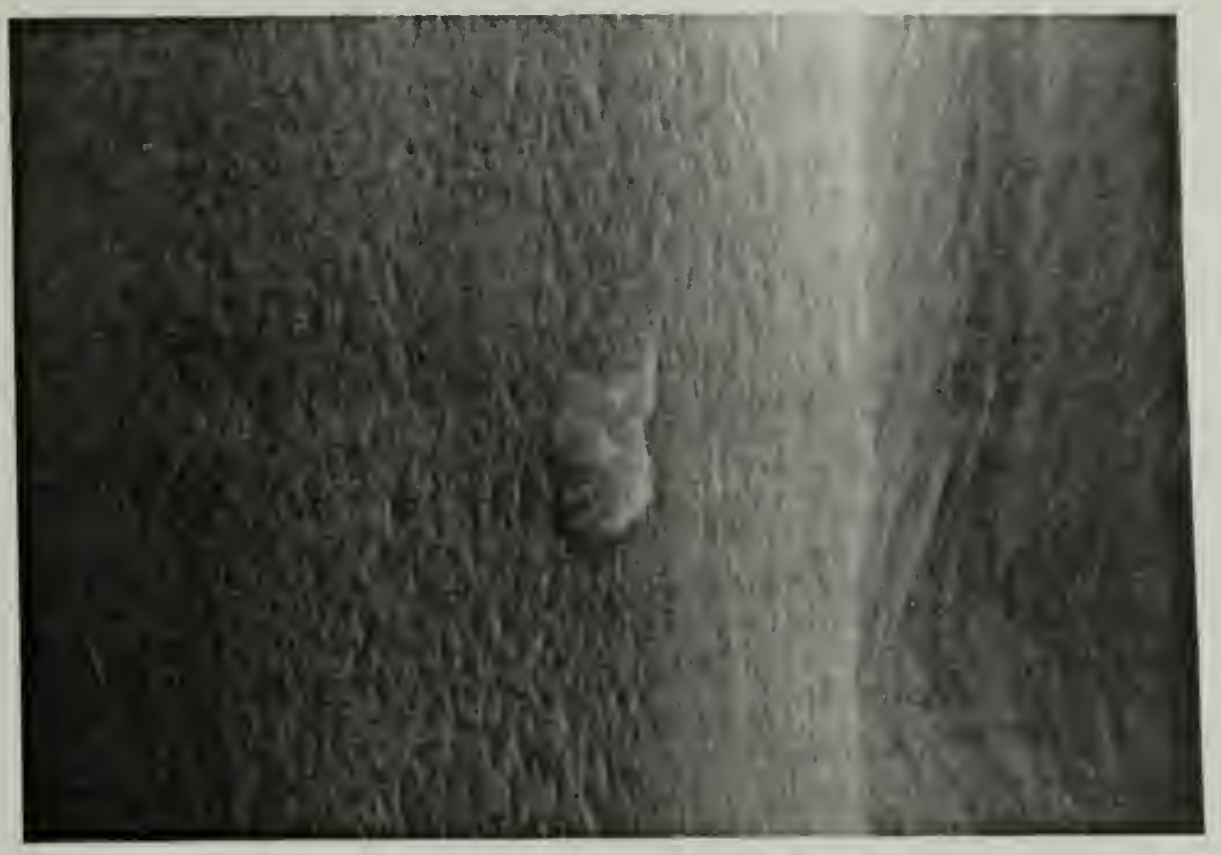


Figure 3.17. SEM micrograph of the solvent etched PET control fiber.

The possibility that the post-treatment improves the mechanical performance of the Triad2 (2:6:7) cannot be completely discounted at this point. Drawing could affect the Triad2 (2:6:7) phase in the following ways: 1) improved orientation of the block copolymer material i.e. a greater number of fibrils with higher aspect ratios may develop, 2) failure of the Triad2 (2:6:7) phase i.e. breakup of the existing fibrils, and 3) the block copolymer may remain unchanged. Unfortunately due to the high degree of crystallinity in the drawn fibers and the similarity of molecular architecture between the two blend components, attempts to distinguish between the phases by solvent etching were not successful. Thus as in the Triad4 systems the Triad2 (2:6:7) block copolymer phase could not be identified in the drawn fibers. Future work will focus on developing a model system to examine the drawing process in these blends and on determining the true mechanism responsible for the reinforcement of the drawn fibers.

3.5 Conclusions

Improving blend compatibility should increase the interfacial adhesion between the different components and thus the mechanical performance. This investigation has focused on using liquid crystalline block copolymers as a means of improving the compatibility between a rigid mesogen and PET. Several different block copolymers have been screened in an effort to determine to optimum molecular architecture necessary to attain good compatibility and ultimately provide reinforcement of PET fibers. Variables that were examined included wt. % rod content, PBT block size and the rigid rod block size.

The quantity of PBT incorporated into the polymer chain had little effect on tensile performance but dramatically influenced the thermal stability. Decreasing the length of the PBT moieties reduced the amount of free shrinkage exhibited by the blended fibers. The length and type of mesogen incorporated influenced both the tensile and thermal behavior of the post-treated systems. The stiffer Triad2 mesogen was more effective than Triad4 at improving the mechanical performance of the fibers particularly when longer mesogenic blocks were used. At the 20 wt. % loading level, the Triad2 systems exhibited both strength and stiffness characteristics significantly greater than the PET control.

Currently the mechanism of reinforcement in the Triad2 blends is unclear. The as-spun fibers did not exhibit any property improvements despite fibrillation of the block copolymer phase. Increases in mechanical and thermal performance were observed only after post-treatment indicating a modification of the PET matrix rather than mechanical reinforcement. Partial miscibility or interaction between the copolymer and PET is considered a possibility since all of the block copolymer could not be accounted for using microscopy, however, evidence of good adhesion between the two phases could not be observed.

Although the mechanism of improvement is currently unknown, it is obvious that the addition of mesogenic block copolymers can significantly enhance the performance of PET. This is an important accomplishment since PET fibers must undergo extensive post-treatment in order to attain the necessary performance characteristics. At comparable loading levels conventional thermotropic LCP's would embrittle the PET matrix to such an extent that post-treatment would not be possible. Another advantage of these block copolymers is the onset of liquid crystallinity at lower temperatures permitting greater processing flexibility. Thus the potential of these materials is high particularly since the processing conditions could not be optimized due to material constraints. By continuing to modify the molecular architecture and processing of these block copolymers, greater improvements in fiber performance are expected.

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CHAPTER 4

TRIAD2 (2:6:7) BLENDED WITH PET AND PC MATRICES

4.1 Introduction

Reinforcement of poly(ethylene terephthalate) (PET) by blending with TLCPs has been attempted by several researchers [1-9]. In some cases the strength and moduli of the PET blends have been found to follow a linear rule mixture leading to substantial increases in material strength and stiffness [4]. The degree of improvement obtained is highly dependent on the processing history of the blends [7]. Studies that subject the melt to a large elongational flow field typically exhibit the greatest property enhancements. However, regardless of processing technique significant increases in modulus and strength are typically not observed until concentrations in excess of 20 wt. percent LCP are incorporated into the blends. At these concentrations, matrix embrittlement is often observed due to incompatibility between blend components. The incorporation of as little as 10 wt. percent LCP usually reduces the elongation of the matrix material dramatically.

The studies conducted thus far in the area of thermoplastic/TLCP blends have focused on improving the properties of extruded or injection molded PET. The modulus of extruded or injection molded PET is relatively low and tends to fall within the 2 to 3 GPa range. It was reasonable therefore to attempt to increase the strength and stiffness of PET by incorporating a high performance TLCP. Unfortunately, due to the nature of these processing techniques, post-treatment or post-drawing of the blends after solidification was not a primary consideration. Investigators typically were not concerned

with the low elongation's to break and matrix embrittlement induced by blending with an LCP. However the mechanical properties of PET can be significantly improved by post-treatment after solidification. Drawing of PET induces crystallization and orientation of the thermoplastic resulting in a substantial increase in mechanical performance. The tensile modulus of high molecular weight PET fibers can attain values in the range of 14 to 17 GPa just by carrying out cold and/or hot drawing post-treatments. The moduli of blended systems, containing 10 to 20 wt percent TLCP, typically do not exceed 5 to 12 GPa. Furthermore, the ultimate strength of neat PET fibers after post-treatment is approximately 1100 MPa, which is significantly greater than PET/TLCP blends incorporating upto 70 weight percent of the TLCP Vectra. Thus if processed correctly the stiffness and ultimate strength of neat PET easily exceeds that of low to moderately concentrated blend systems that cannot be post-treated.

If the compatibility between PET and a TLCP reinforcement material could be sufficiently increased to permit post-drawing, the mechanical properties of these blend systems should increase dramatically. Improved stiffness, strength and toughness would be expected since the properties of the PET matrix would increase by an order of magnitude. A better matrix material would improve the efficiency of the reinforcement phase since less TLCP would be needed to obtain moderate stiffness values. Enhanced compatibility could also result in better adhesion between the polymers along with greater processing flexibility. In addition to the melt techniques of extrusion and injection molding, processes requiring solid state drawing such as biaxially oriented film formation and fiber spinning could be performed.

In the previous chapter the possibility of improving upon the properties of neat PET fibers by incorporating novel TLCP block copolymers was investigated. One particular block copolymer system exhibited a 40 % increase in fiber modulus without causing matrix embrittlement. Even at a concentration of 20 wt. percent TLCP the blended fibers could still be easily post-treated using conventional fiber processing methods. However,

the mechanism of reinforcement provided by the block copolymer was unclear. The as-spun fibers did not exhibit any significant property improvements despite fibrillation of the LCP phase. Increases in mechanical and thermal performance were observed only after post-treatment, indicating a modification of the PET matrix material had occurred rather than true mechanical reinforcement by the LCP phase. Partial miscibility or interaction between the copolymer and the PET matrix was also considered a possibility since all of the LCP could not be accounted for by scanning electron or optical microscopy.

The objective of this study was to determine whether the LCP modified the PET matrix phase or provided true mechanical reinforcement of the fiber. Since the block copolymer was specifically engineered to be compatible with PET, a model system using a polycarbonate matrix has been designed to elucidate the mechanism of property enhancement. Fiber compositions containing 20 wt. percent TLCP are compared. The fibers are prepared by melt extrusion followed by cold drawing. In the PET systems, the fibers are also hot drawn to maximize performance. The fibers are tested for tensile performance and dimensional instability.

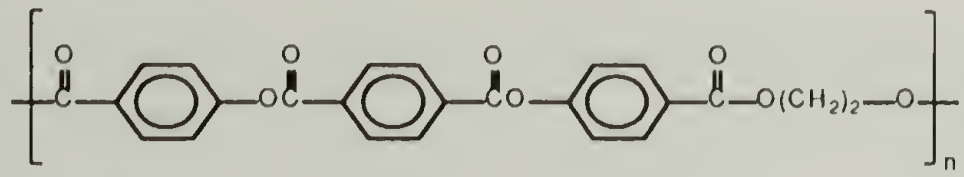
4.2 Materials

The fiber grade PET used in this study was kindly provided by the Akzo Corporation. The material had a reported melting transition of 273°C and an inherent viscosity of 2.04 (dL/g). The PET was blended as received without further purification.

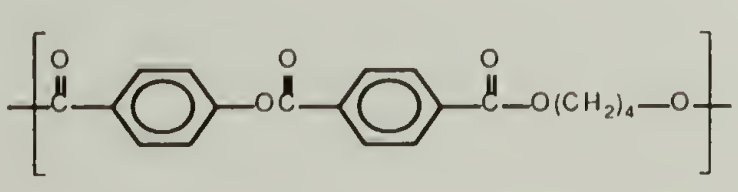
The PC used in this study is sold under the trade name Merlon M-50 (H) and was kindly provided by the Bayer Corporation. A glass transition of 143°C was determined by differential scanning calorimetry using a heating rate of 20°C/min. The pellets exhibited an inherent viscosity of 0.55 (dL/g) as measured at a concentration of 0.25 % in dioxane at 30°C. The PC was also blended as received without further purification.

The thermotropic LCP used in this study was a novel block copolymers kindly synthesized by Drs. Lenz and Kantor's group at the University of Massachusetts, Amherst [10]. The LCP is a segmented block copolymers consisting of rigid-rod, diad, and flexible coil segments. Figure 4.1 shows a schematic of the general structures incorporated into the block copolymer. The mesogenic segments consists of six poly(dimethylene-4,4' terephthaloyl dioxydibenzoate) (Triad2) units. The flexible coil segment is composed of seven poly(butylene terephthalate) (PBT) units. Furthermore, due to the reaction scheme chosen to synthesize these copolymers, tetramethylene-4.4' dioxydibenzoate (Diad4) sequences are incorporated between the rigid-rod and flexible coil segments. These diads are known to be mesogenic [11].

Triad2 Mesogenic Block



Diad4 Unit



PBT Flexible Block

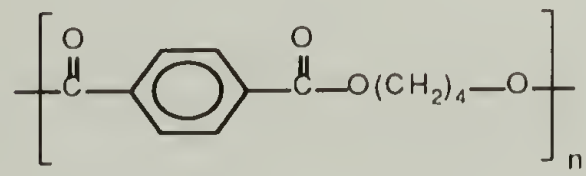


Figure 4.1. Structural moieties incorporated into the TLCP alternating block copolymer.

The block copolymer, shown in figure 4.2, has been designated Triad2 (2:6:7) corresponding to the 2 Diad4 units connecting Triad2 and PBT blocks having segment

length of 6 and 7 units respectively. The amount of material available for blending and property determination was limited, thus the mechanical properties of the neat copolymer could not be determined.

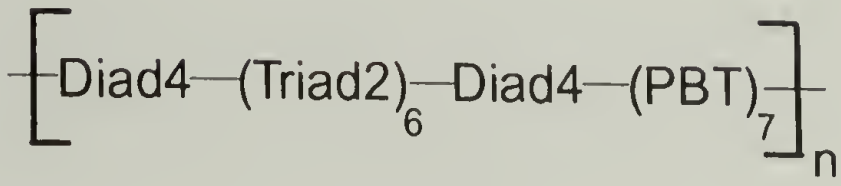
Block Copolymer	Copolymer Structure
Triad2 (2:6:7)	

Figure 4.2. Triad2 (2:6:7) alternating block copolymer chemical structure.

4.3 Experimental

4.3.1 Thermal Characterization

The transition temperatures of the neat materials and the blends were measured calorimetrically using a TA Instruments 9900 differential scanning calorimeter. Temperature calibration was performed using an indium standard. Samples of approximately 10 mg were initially heated in a nitrogen atmosphere from 30 to 300°C at a heating rate of 20°C/min, followed by quenching with liquid nitrogen. Samples were then reheated to 300°C at a heating rate of 20°C/min. The reported transitions are the maximum peak temperatures observed during the second heating run.

4.3.2 Fiber Formation

Powders of the thermotropic polyesters and the respective matrix material were tumble mixed for 24 hr's. The amount of block copolymer used in the extruded blends

was 20 % by weight. The mixed polymer powders were then compression molded using a Carver laboratory press at 270°C for 1 minute. The compressed sample was consequently ground in an analytical mill to a particle size less than 1000 microns and vacuum dried at 120°C for a minimum of 24 hours. Compression molding followed by grinding was convenient for obtaining particles that effectively fed into the mini-extruder.

Once thoroughly dried, the blends were extruded and spun into fibers. Extrusion was carried out with a ¼ inch Randcastle single screw mini-extruder. The mini-extruder has four temperature zones which may be varied independently. The feeding, compression and melting sections, zones one, two and three respectively, were set at 220°C, 260°C and 280°C. The temperature of the die zone was also set at 280°C for both the PET and the PC blends. The ability to obtain a uniform melt without die swell was the main criteria for determining the die temperature. The screw speed was held constant at 30 rpm corresponding to an extrusion rate of 1.5 g/min and a polymer residence time of two to four minutes within the extruder. The residence time in the extruder was kept to a minimum in order to reduce the possibility of transesterification reaction between the blend components.

Upon exiting the die of the extruder, the polymer was stretched using a custom built take-up device. A take up speed of either 75 or 225 m/min was used for all systems. The stretch ratio for each system was determined as the ratio between the die and the drawn extrudate cross-sections (A_0/A_f). The round hole capillary die had a diameter of 1575 μm and an aspect ratio of ten. Fiber diameters were determined by optical microscopy.

A two step post-treatment process was performed on the PET blends immediately following the spinning process. The heat treatment of poly(ethylene terephthalate) fibers is an important processing stage that determines the ultimate properties of the material. Post drawing was accomplished using a continuous process between optoelectronically monitored feed and take-up spools. Cold drawing was performed at 85°C using a standard laboratory hot plate. The speed of the feed spool was kept constant at 5 m/min

while the speed of the take-up winder was continuously monitored and increased until a stable neck was observed. For neat PET this occurred at a draw ratio of 3.5.

Hot drawing of the PET systems was accomplished using a similar procedure at a temperature of 205°C. The maximum draw ratio was determined by slowly increasing the speed of the take-up spool until excessive filament breakage occurred. The speed of the take-up spool was then decreased until drawing could proceed for at least two minutes without filament breakage. For neat PET this corresponded to a maximum hot draw ratio of 1.5 and a total draw ratio of 5 for the fiber. The total draw ratio was calculated as the ratio between the as-spun and final post-treated fiber cross-sectional areas. All samples were collected and tested at the maximum draw ratio unless otherwise specified.

Since PC is an amorphous material the fibers could not be hot drawn, thus the post-treatment of the PC fibers consisted of a single drawing step performed at 85°C. The cold drawing of the PC and PET systems were performed in an identical manner. The final draw ratio obtained for the PC systems was approximately 2. Pertinent fiber processing information is summarized in Table 4.1

Table 4.1. Fiber processing results.

	Spun Diam. (μm)		Stretch Ratio		Drawn Diam. (μm)	Draw Ratio
	75m/min	225m/min	75m/min	225m/min	75 m/min	75 m/min
PET	86	64	335	600	38	5.1
20 % Triad2 (2:6:7)/PET	84	60	350	680	36	5.5
PC	74	40	450	1520	57	1.7
20 % Triad2 (2:6:7)/PC	82	42	370	1400	56	2.1

4.3.3 Tensile Testing

Tensile tests were performed on an Instron 1113 tensile tester connected to a personal computer. Specimens were mounted with an adhesive onto paper tabs to facilitate mounting and alignment. Fiber diameters were measured using an Olympus microscope equipped with a calibrated scale accurate to $\pm$ 0.5 microns. A minimum of five diameter measurements per fiber were obtained. The applied strain rate was 10 percent elongation per minute, with an initial gage length of 50 mm. A 550g Toyo TI550 load cell was used to measure the fiber load. The Young's modulus was determined from the best linear fit through the initial region of the stress-strain curve. Instrument compliance was measured and found to be approximately 2 percent. Sample that exhibited grip failure were omitted from the tenacity and ultimate elongation results. Each tensile property was averaged over nine tests and performed at ambient conditions in the laboratory. Standard deviations ranged from 5 to 10 percent.

4.3.4 Thermal Instability

Shrinkage experiments were performed by placing the fibers in a convection oven preheated to the desired temperature 15 minutes. The preheat temperatures were 190°C and 130°C for the PET and the PC systems respectively. Prior to heating the fibers were conditioned for 24 hours at 21°C and 68 % relative humidity. The sample lengths before and after heating were determined at ambient temperature by straightening the fibers with a small load and measuring the initial (L_0).or final (L_1) length respectively. All samples were approximately 20 cm in length before testing. After removal from the oven, the fibers were reconditioned for one hour and the resultant dimensional changes determined.

The free shrinkage was computed as

$$[\%] = (L_0 - L_1)/L_1 * 100.$$

Shrinkage values were averaged over 5 measurements.

4.3.5 Morphology

The morphology of the blends was investigated by optical microscopy (OM) and scanning electron microscopy (SEM). The as-spun PET fibers were solvent etched using a 60/40 parachlorophenol tetrachloroethane mixture to remove the PET matrix phase. The solvent mixture was slowly dropped onto the fibers at 5 ml per minute for approximately 1 minute. The PC samples were prepared in an analogous manner except the etching solvent was methylene chloride. All SEM samples were mounted on aluminum stubs, sputtered with gold using an SPE Sputter Coater, and characterized using a JEOL [JSM-35C] scanning electron microscope. An accelerating voltage of 20 kv was used. An Olympus microscope was used for observing the blends before and after processing.

4.4 Results and Discussion

4.4.1 Thermal Characteristics

The DSC traces of the PET blends and the pure components are shown in figure 4.3. As discussed in the experimental section these are second heating scans, 20°C/min, performed after a liquid nitrogen quench from 300°C. The relevant numerical data from the DSC measurements are collected Table 4. 2. The enthalpies of fusion and crystallization for the blends are normalized to the PET content.

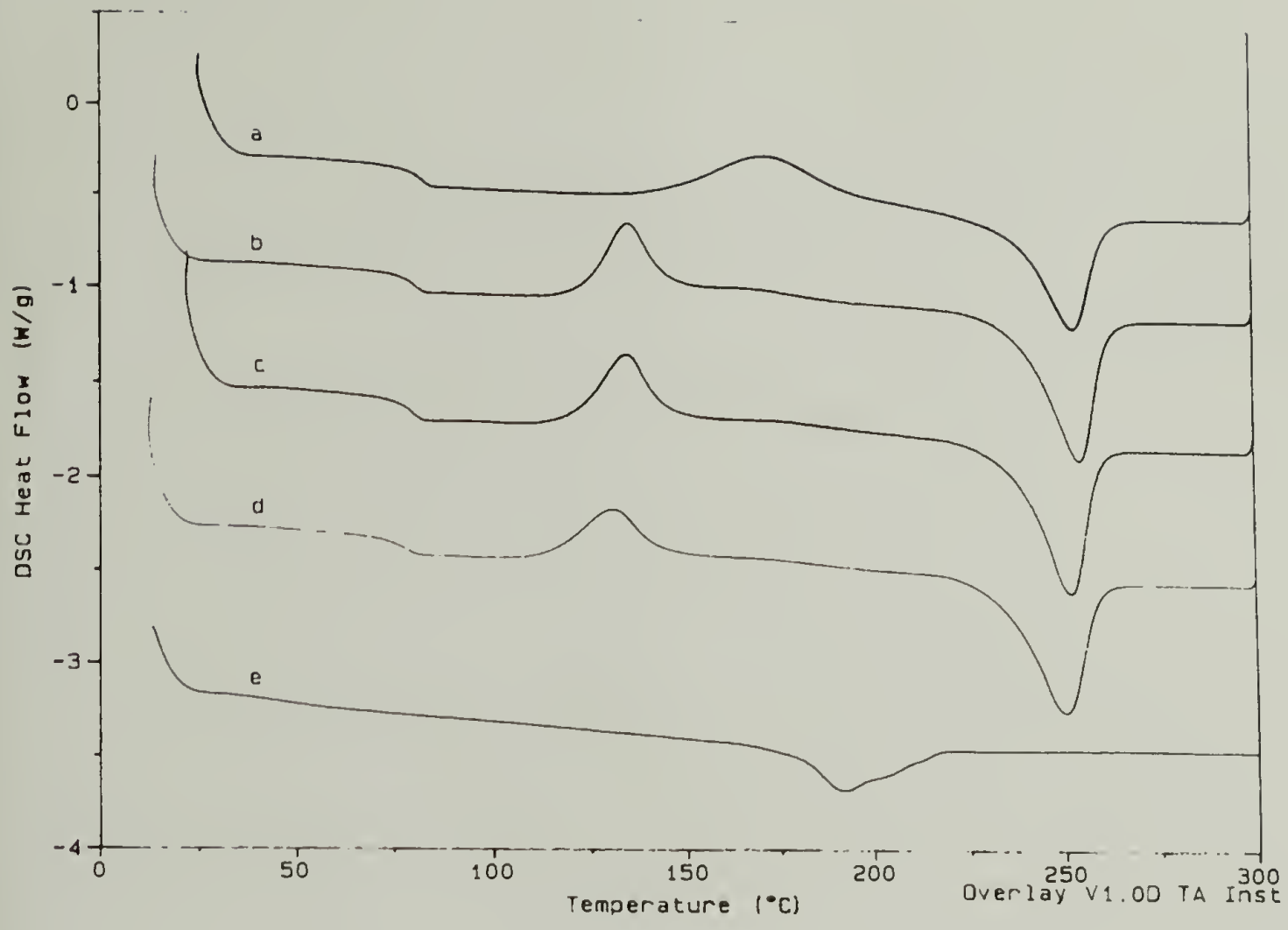


Figure 4.3. DSC second heating scans a) Neat PET, b) 5% Triad2 (2:6:7)/PET, c) 10% Triad2 (2:6:7)/PET, d) 20 % Triad2 (2:6:7)/PET, e) Neat Triad2 (2:6:7)

Table 4.2. Numerical data determined from DSC measurements of PET blend systems.

	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PET	82.4	171.2	23	252.8	29
5% Triad2 (2:6:7)	81.5	134.5	16	253.9	37
10% Triad2 (2:6:7)	80.1	134.3	17	251.5	41
20% Triad2 (2:6:7)	77.6	130.7	18	249.8	46
Triad2 (2:6:7)			17	193	

The heating trace of the neat, as supplied PET sample (curve a) is characterized by a well defined glass transition at 82°C (T_g). An exothermic cold crystallization peak (T_c) and melting endotherm (T_m) are also visible at 171 and 253°C respectively. A comparison of the heat of crystallization (ΔH_c) and the heat of fusion (ΔH_m) suggests that the PET did not crystallize to a significant extent during the liquid nitrogen quench.

The DSC scan of the neat Triad2 (2:6:7) (curve e) shows an endothermic peak at 193°C (T_m). Following this transition the material is biphasic i.e. it exhibits both isotropic and nematic phases until the onset of degradation at 336°C. See figures 4. 4 and 4. 5. The absence of a cold crystallization peak indicates that all of the crystallization occurred during the liquid nitrogen quench. Furthermore the lack of a well defined glass transition and a small heat of fusion are common characteristics of thermotropic liquid crystalline polymers [12, 13].

Curves b-d in figure 4. 3 are the DSC traces for the PET-LCP blends. Surprisingly the melting endotherm of the LCP minor component could not be observed in any of the systems, however, the addition of small amounts of LCP does have a profound effect on the thermal behavior of the blends. All of the blends exhibit a glass transition, but the

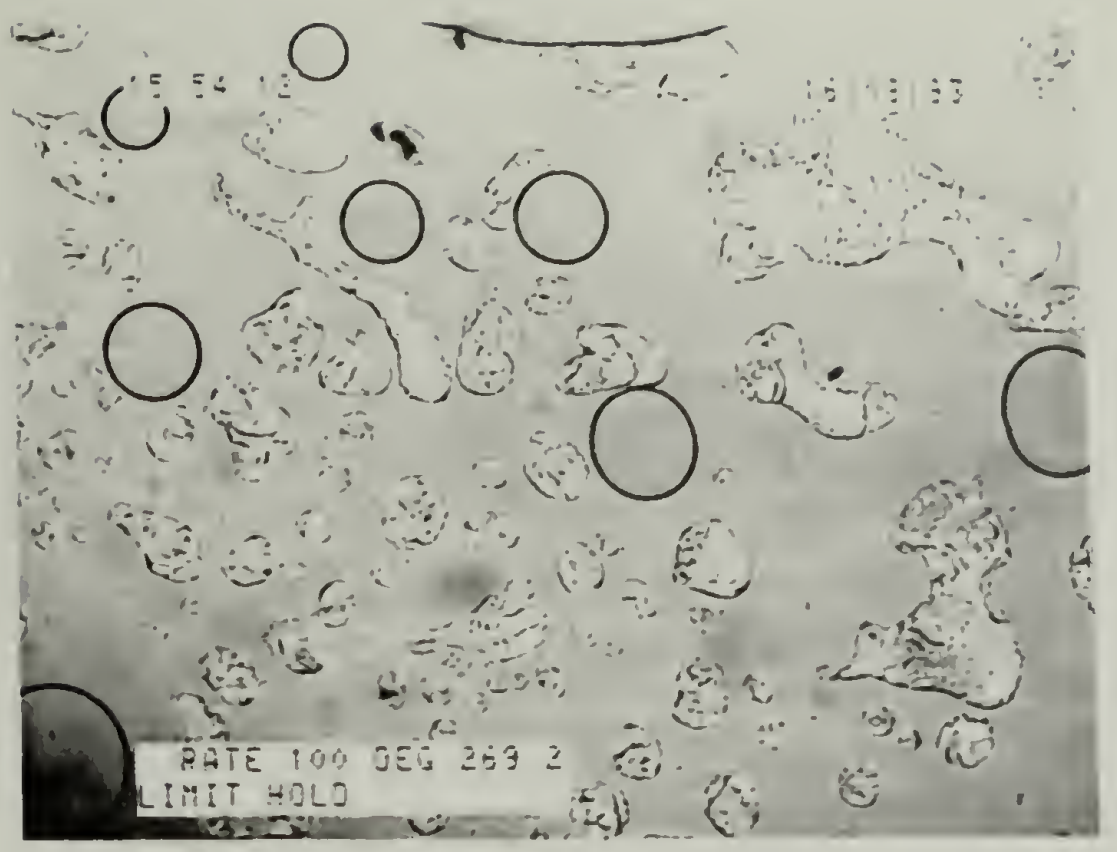


Figure 4.4. The 20% Triad2 (2:6:7)/PET blend powder observed prior to extrusion with an optical microscope equipped with a hot stage. The blend has been magnified 100 times and heated to 270°C.

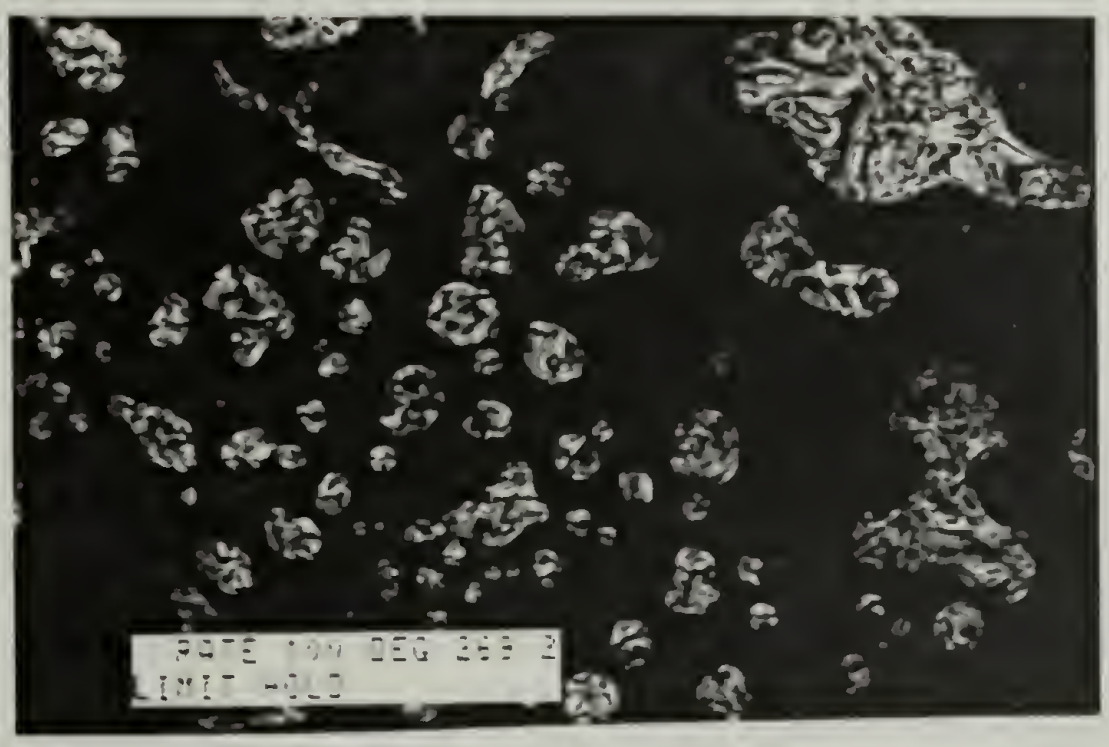


Figure 4.5. The 20% Triad2 (2:6:7)/PET blend powder observed prior to extrusion with an optical microscope equipped with a hot stage. The blend has been magnified 100 times, heated to 270°C and observed with crossed polarizers

temperature of this transition is dependent upon the concentration of LCP incorporated into the blend. As the concentration of LCP was increased from 0 to 20 % the T_g's decreased from 83°C for neat PET to 77°C for the 20% blend. This result suggests that some interaction between the blend components may have occurred. It is also interesting to note that the temperature of the transition was reduced indicating that the glass transition of Triad2 (2:6:7) is lower than neat PET. This is not unreasonable since the block copolymer contains a significant amount of PBT, which typically exhibits a T_g around 55°C and is miscible with PET.

The addition of Triad2 (2:6:7) also affects the cold crystallization temperature of PET. In all of the blended systems PET undergoes cold crystallization approximately 35° C lower than the neat PET. Although this phenomena does not exhibit any clear concentration dependence, the 20 % system does exhibit the greatest temperature reduction in PET cold crystallization. The enthalpies of crystallization, normalized to the PET content, were essentially independent of Triad2 content but a slight reduction was observed for all of the blends. Conversely the heat of fusion is seen to dramatically increase with Triad2 (2:6:7) content. This is an indication that the extent or degree of PET crystallinity was significantly increased by the addition of Triad2 (2:6:7). Assuming that the enthalpy of fusion of 100 % crystalline PET is of 140 J/g [14, 15], the degree of crystallinity increased from 21 % for neat PET to approximately 32 % for the 20 % Triad2 (2:4:6) blend. Other investigators have observed similar phenomena in other LCP-random coil systems but typically to a lesser degree than observed here [7, 16]. The increase in crystallinity is often attributed to the LCP performing as a nucleating agent for the PET.

4.4.2 Tensile Performance

The effect of adding 20 wt. % Triad2 (2:6:7) on the Young's modulus of as-spun PET and PC is shown in figure 4.6. The controls and the blends were spun using identical

temperature profiles i.e. a die zone temperature of 280°C was used for all sample preparation. Take-up speeds of 75 and 225m/min were used to determine the effect of elongational flow on mechanical performance.

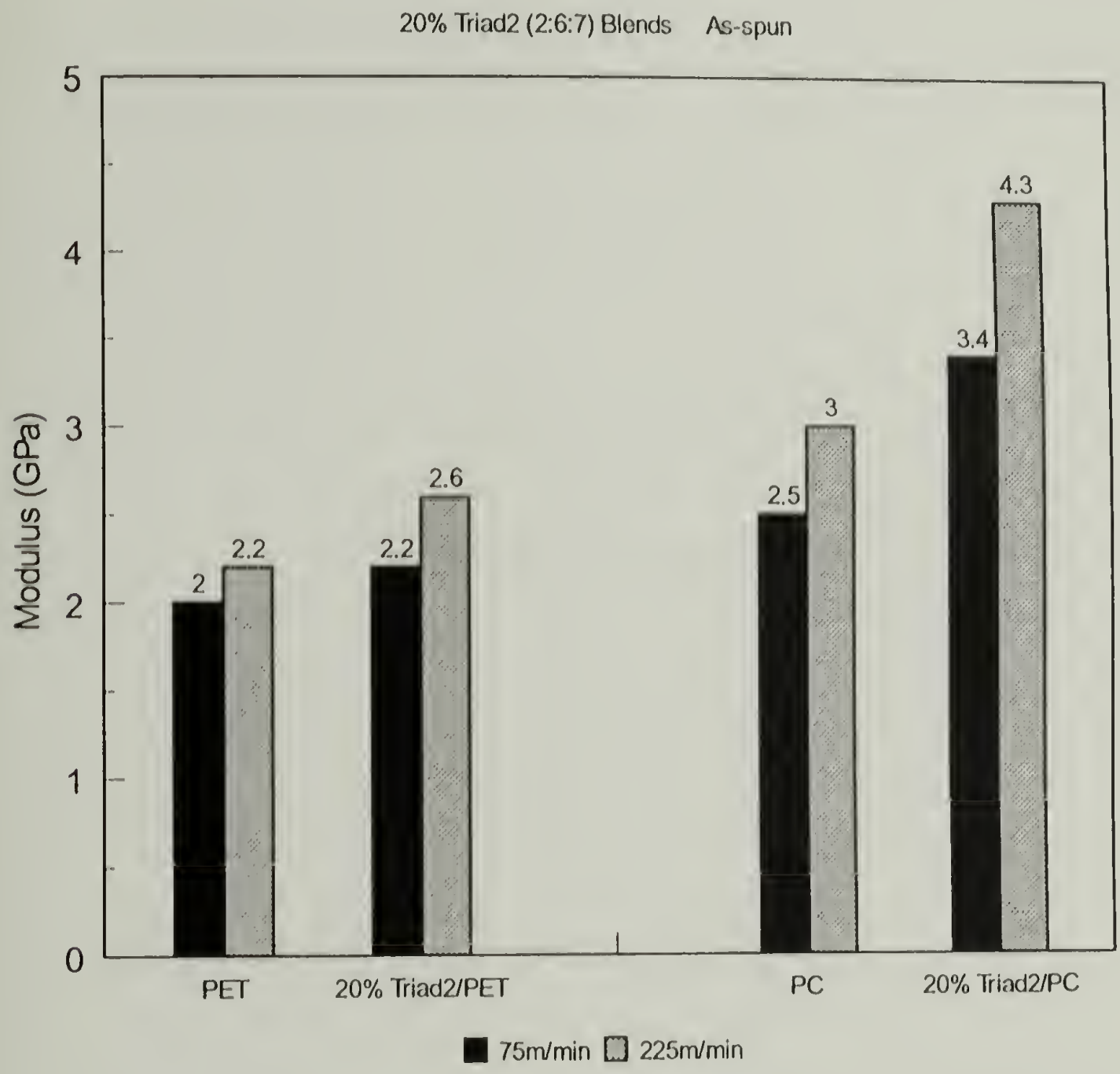


Figure 4.6. As-spun fiber modulus values for the Triad2 (2:6:7) blends and controls.

The modulus of the PET control was essentially independent of the take-up speed and the addition of 20 % Triad2 (2:6:7) to PET does not significantly enhance the mechanical performance of the thermoplastic. A slight increase in modulus, 0.4 GPa, was observed when the take-up speed was increased to 225 m/min, but this was not considered significant.

Adding 20 wt. % Triad2 (2:6:7) to PC improved the modulus of the samples by approximately 1.0 GPa. The degree of enhancement was dependent upon take-up speed with the higher speed, 225m/min, leading to a greater amount of reinforcement. If the general rule of mixtures is used to estimate the modulus of the neat Triad2 (2:6:7) a value of approximately 9 GPa is obtained. This result is comparable to the 13 GPa modulus obtained by Shin and Chung [6], although a different flexible spacer group was investigated.

Thus the incorporation of flexible moieties into the LCP chain may promote interaction between the blend components, but this does not necessarily lead to mechanical reinforcement of the system. For instance DSC results indicate that some interaction occurs between PET and Triad2 (2:6:7), but there is no evidence of any substantial mechanical reinforcement. Conversely the PC blends do exhibit mechanical reinforcement, but the incorporation of flexible units appears to have reduced the modulus of the block copolymer significantly. Furthermore, compared to more rigid TLCP's the amount of reinforcement observed in the PC blend is not dramatic [17].

After spinning the fibers were post-treated as described in the experimental section. Post-treatment was performed on the fibers taken up at 75 m/min. The PET systems were cold and hot drawn whereas the PC systems were only cold drawn since the Tg of the PC prohibited high temperature drawing. The mechanical properties of the blends after post-treatment are shown in figure 4. 7.

The results of the PET blended with 20 % Triad2 (2:6:7) were surprising. After post-treatment a significant improvement in mechanical performance was observed i.e. the modulus was increased from 17 to 24 GPa compared to the PET control. This was unexpected since mechanical reinforcement was not observed in the as-spun PET blend. Furthermore, the post-treated PC systems did not exhibit any significant differences in mechanical performance. The PC control and the 20 % Triad2 blend had moduli of

approximately 4.5 GPa. Thus the modulus enhancement observed in the as-spun PC blend wasn't improved upon by post-drawing.

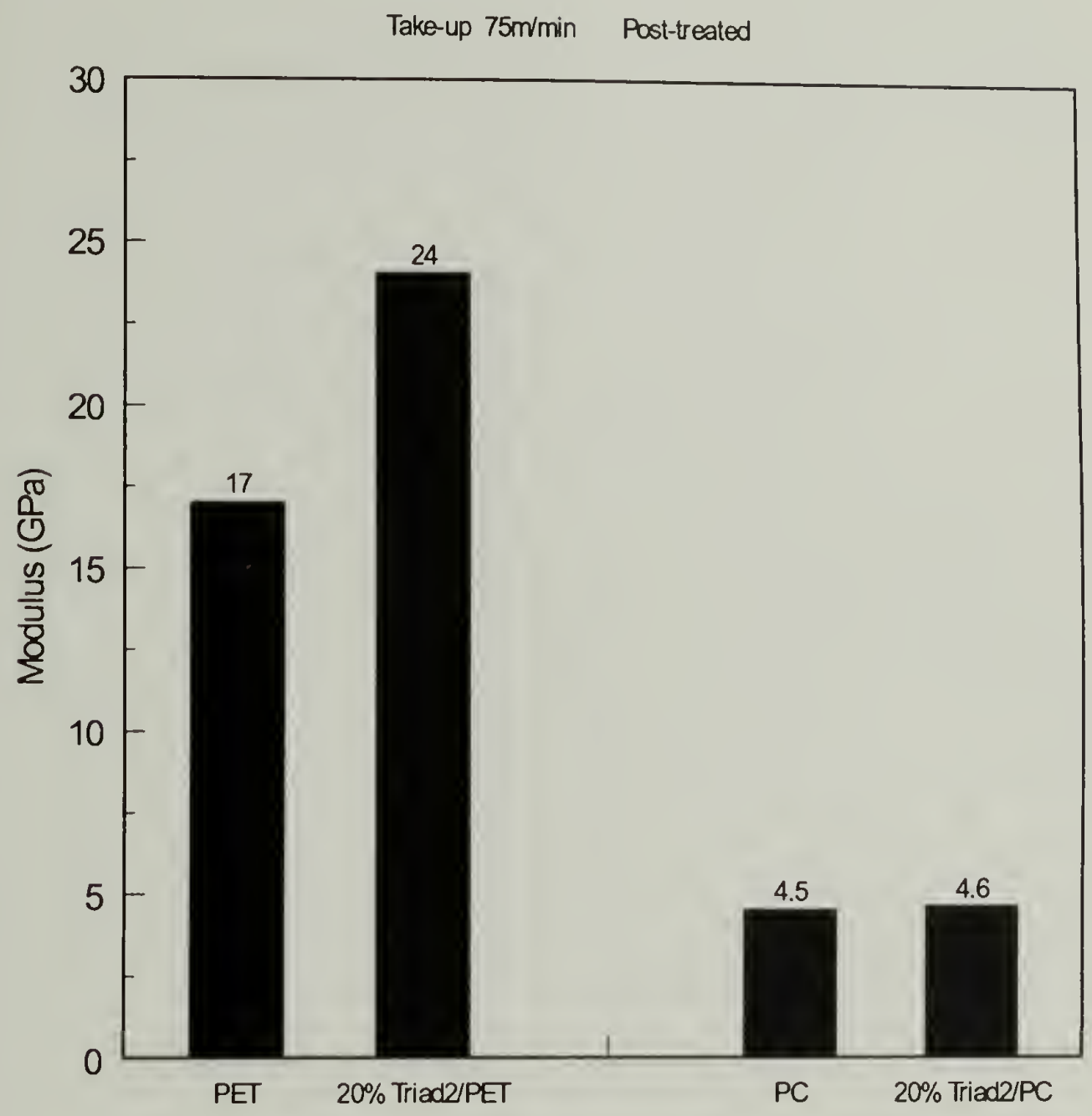


Figure 4.7. Post-treated modulus values for the control and 20% Triad2 (2:6:7) fiber blends.

Thus the addition of the Triad2 (2:6:7) block copolymer appears to have dramatically different effects depending upon the selected matrix polymer. In the PET blend, fiber enhancement wasn't observed until after post-treatment; whereas in the PC blend system post-drawing negated the as-spun fiber modulus increases. This result suggests that different mechanisms of reinforcement may be responsible for the

improvements observed in the respective matrix materials. For instance the DSC results indicate that the Triad2 could be modifying the PET matrix by influencing the fiber's crystallization behavior. Since PET crystallization is not induced until the post-treatment step, performance improvements would not manifest until after this processing stage. Conversely, in the as-spun PC blend system the LCP may provide true mechanical reinforcement analogous to conventional fiber reinforced composites. Subsequently, a significant increase in the mechanical performance of the PC matrix material, due to induced orientation during the post-drawing process, could effectively negate any modulus enhancements obtained in the as-spun fibers. This would be particularly likely if the modulus of the Triad2 (2:6:7) block copolymer was only on the order of 10 GPa.

Another possibility is that the post-treatment process improves the mechanical performance of the Triad2 (2:6:7) block copolymer. However, this is thought to be unlikely since the effect should be identical for both matrices and not material dependent.

4.4.3 Dimensional Instability of the Triad2 (2:6:7) Blends

Free shrinkage experiments were performed on the post-treated fibers. The tests were performed as described in the experimental section, but the maximum temperature for each system varied depending upon the matrix polymer. The PET systems were heated to 190°C while the PC systems only experienced a maximum temperature of 115° C. It was hoped that by incorporating a thermotropic LCP the thermal stability of the matrix polymer could be improved. The results are shown in figure 4.8.

The neat PET and PC fibers exhibited free shrinkage's of 10 and 15 percent respectively. The PET fiber shrinks significantly less than the PC due to the large extent of crystallinity in the fiber [18]. The free shrinkage of the blend fibers are significantly different. The addition of 20 % Triad2 (2:6:7) to PET slightly improved the free shrinkage behavior of the fiber from 9 to 7 percent. However, the PC blend system

exhibited 30 percent shrinkage which was double the amount of the neat PC fiber. Thus the ability of Triad2 to alter thermal behavior also appears to be dependent upon the matrix material.

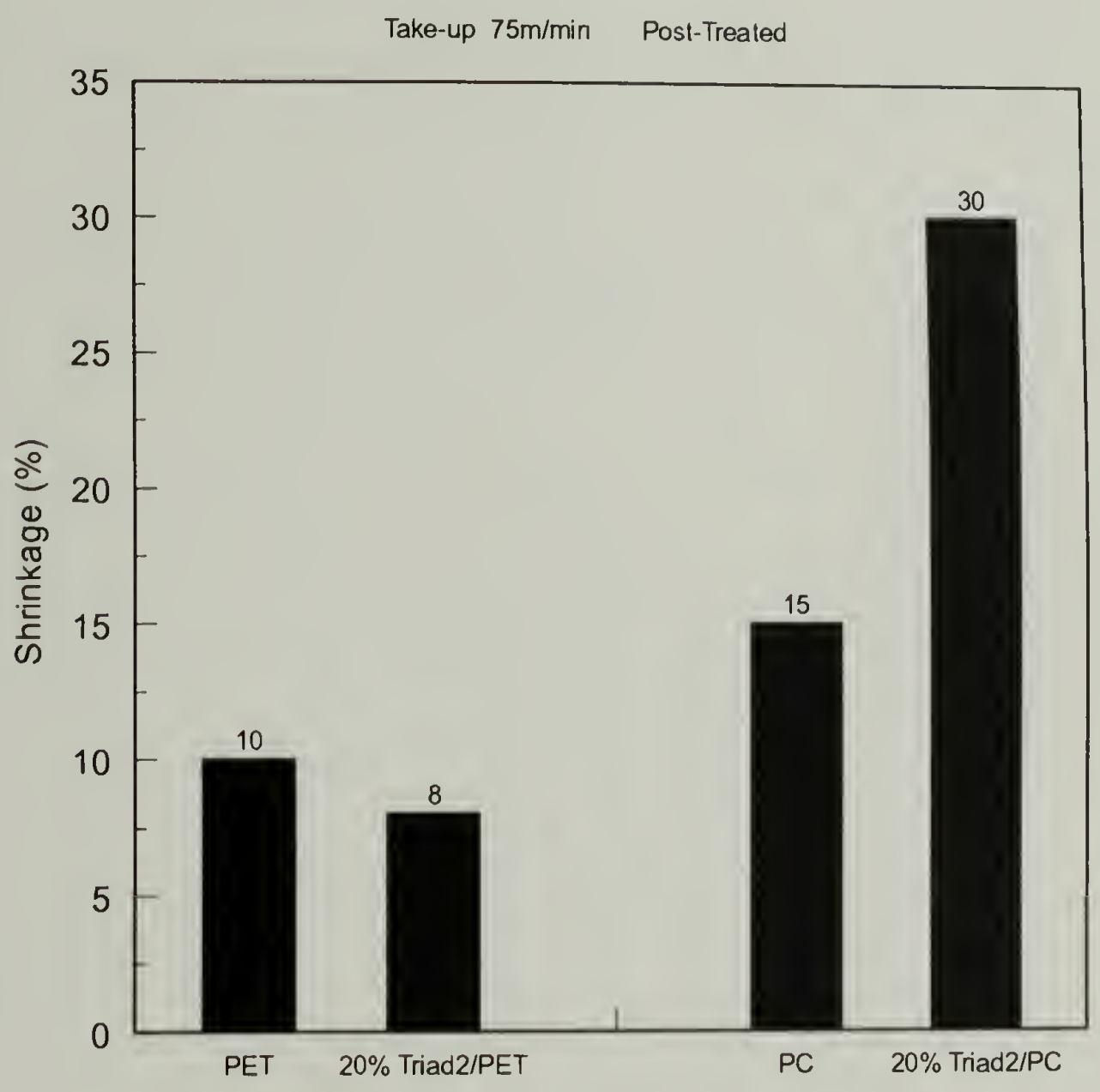


Figure 4.8. Dimensional instability of the control and 20 % Triad2 (2:6:7) fiber blends.

Although the addition of the Triad2 (2:6:7) block copolymer did not reduce the free shrinkage of the PC matrix, the results offer further evidence that different reinforcement mechanisms are responsible for fiber improvements. If the degree crystallinity in the PET were improved through matrix modification, the amount of free shrinkage experienced by the fiber would be expected to decrease. In the case of true mechanical reinforcement, the Triad2 block copolymer would have to essentially anchor the PC matrix in place in order

to reduce shrinkage. This phenomena has been observed by Nicolais and coworkers [19] in polystyrene systems blended with the TLCP Vectra. The dramatic increase in shrinkage for the PC blend fiber indicates that the dimensional instability of the Triad2 block copolymer may be significantly greater than the PC matrix material. This result was unfortunate but reasonable since a significant portion of poly(butylene terephthalate) was incorporated into the block copolymer.

4.4.4 Morphology of the Triad2 (2:6:7) Blends

In order to elucidate the geometry of the Triad2 phase within the respective matrices, the as spun fibers were solvent etched and observed using optical and scanning electron microscopy. The PET systems were etched using a 60/40 mixture of parachlorophenol to tetrachloroethane while methylene chloride was used for the PC systems. Figures 4.9 and 4.10 are optical micrographs of the remaining residue after etching the PET and PC as-spun fibers respectively. The presence of Triad2 fibrils are clearly evident in both blend systems, however, the number of fibrils and their aspect ratios were dramatically different. Figures 4.11 and 4.12 are SEM micrographs of the etched fibers. Figure 4.11 shows a single Triad2 fibril oriented along the PET fiber axis, whereas figure 4.12 reveals a tremendous quantity of Triad2 fibrils oriented along the fiber direction. The diameters of the fibrils in the PET system ranged from 1 to 1.5 μm with aspect ratios varying from 25 to 160. These aspect ratios are considerably smaller than those observed in the PC system which appear to be essentially infinite. The diameters of the fibrils within the PC are very non uniform and range from 0.2 to 1.0 μm. In addition the fibrils appear to have formed an infinite network within the PC matrix.

Figure 4.9. Etched 20 % Triad2 (2:6:7)/PET as-spun fiber magnified 500 times using optical microscopy. Micrograph depicts fibrils of Triad2 (2:6:7) phase with various aspect ratios.

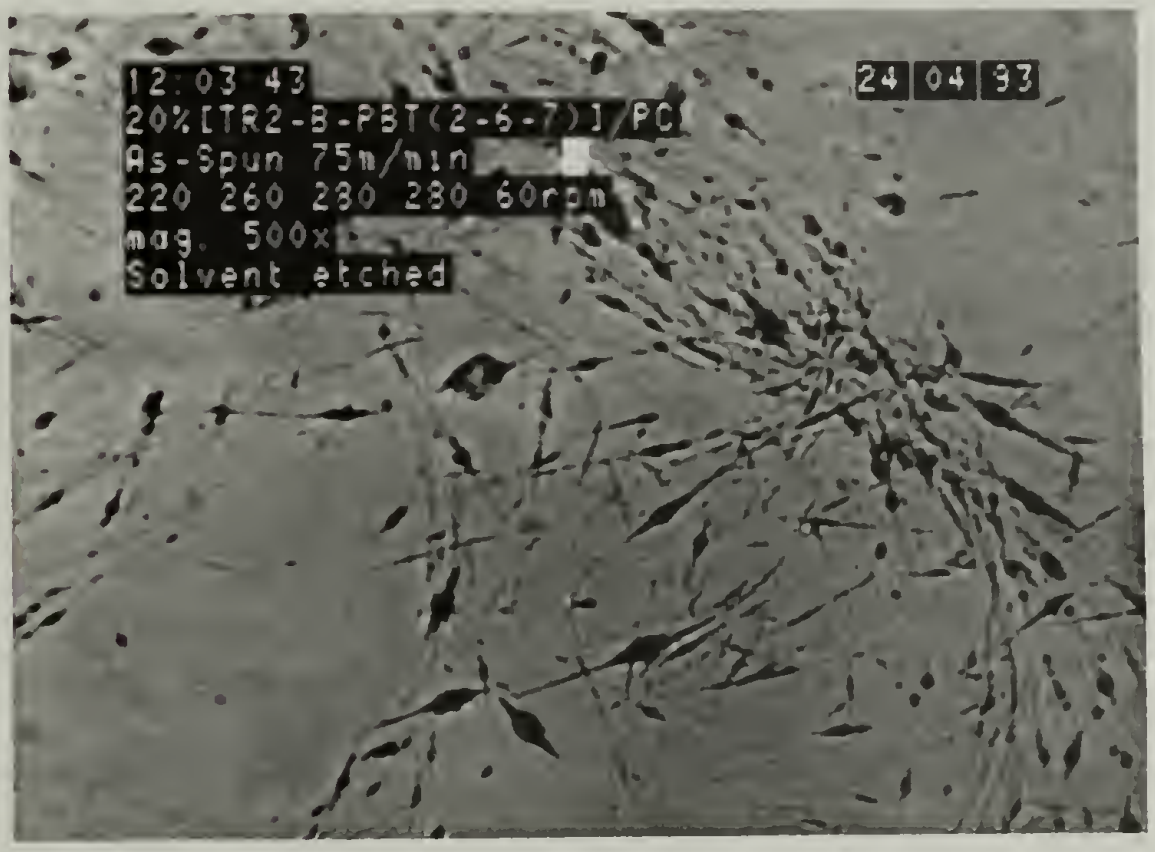


Figure 4.10. Etched 20 % Triad2 (2:6:7)/PC as-spun fiber magnified 500 times using optical microscopy. Micrograph depicts fibrils of Triad2 (2:6:7) phase having high aspect ratios and varying diameters.

Figure 4.11. Etched 20 % Triad2 (2:6:7)/PET as-spun fiber magnified 5000 times using scanning electron microscopy. Micrograph depicts a single fibril of the Triad2 (2:6:7) phase.

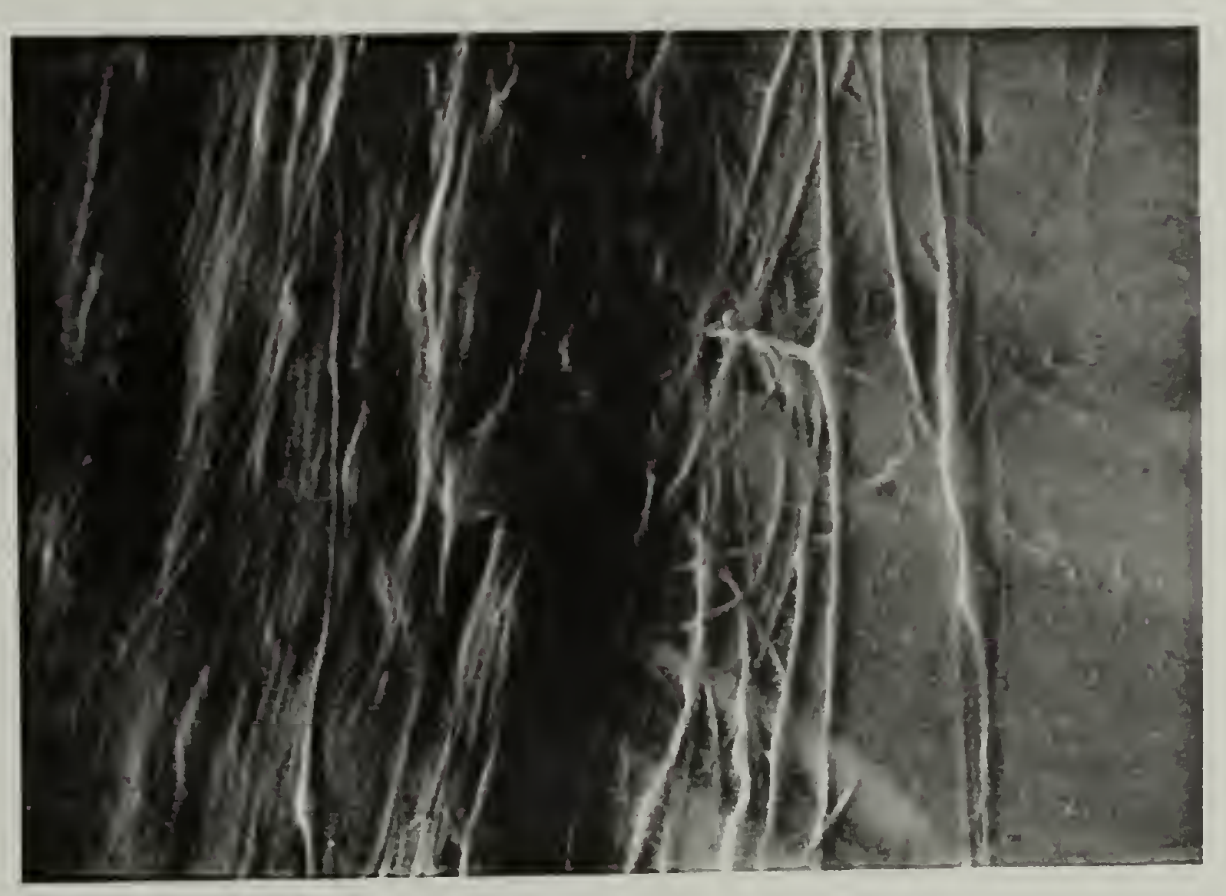


Figure 4.12. Etched 20 % Triad2 (2:6:7)/PC as-spun fiber magnified 5000 times using scanning electron microscopy. Micrograph depicts fibrils of Triad2 (2:6:7) phase having high aspect ratios and varying diameters.

The disparity in the number of fibrils observed in the PET and PC blends indicates that the Triad2 block copolymer may be partially miscible with the PET matrix and/or the geometry of the LCP phase may have been predominately particulate. Partial miscibility of the Triad2 with the PET matrix could make fibril generation difficult [7], and a particulate morphology would not be readily visible with optical microscopy since particulates would be susceptible to removal during the etching process.

The morphologies of the as-spun fiber blends further indicate that the Triad2 block copolymer performs as a matrix modifier for PET and as a poor reinforcement material for PC. The number of fibrils observed in the PET blend would not be sufficient to improve the mechanical performance of the system as indicated by the tensile results. In addition all of the Triad2 phase cannot be accounted for at this point suggesting that some interaction with the PET may have occurred as indicated by the DSC results.

The morphology of the PC system reveals a large number of high aspect Triad2 fibrils aligned along the direction of the fiber axis. This type of morphology is considered to be ideal for obtaining the maximum reinforcement potential from the Triad2 phase. Indeed some modulus improvement was observed in the as-spun fibers, however the increase was moderate at best. Thus the inherent mechanical properties of the Triad2 do not appear to be extremely high. Furthermore, the estimate of 9 GPa obtained using the simple rule of mixtures is considered a reasonable approximation.

Figure 4.13 is an optical micrograph of a solvent etched PC blend fiber after post-treatment. The fiber has been magnified 200 times and observed using crossed polarizers. It is immediately obvious that the Triad2 fibrils are highly birefringent and oriented along the fiber direction. There is also an apparent fracture of the Triad2 fibrils across the entire fiber cross section. These fibril fractures are periodic and occur along the fiber axis approximately every centimeter. This observation indicates that fiber post-drawing breaks up the Triad2 fibrils within the matrix. Fracture of the Triad2 phase decreases the fibril aspect ratio and essentially reduces the ability of the LCP to mechanically reinforce the

matrix material. This results suggests that it is unlikely that post-drawing improves the mechanical performance of the Triad2 material. Therefore the absence any modulus enhancement in the post-treated PC blends can be attributed to an improved PC matrix. The drawing procedure effectively orients the PC matrix material but doesn't increase the performance of the Triad2 phase. After post-drawing the Triad2 mechanical properties are not sufficient to improve upon the performance of the drawn PC matrix material.

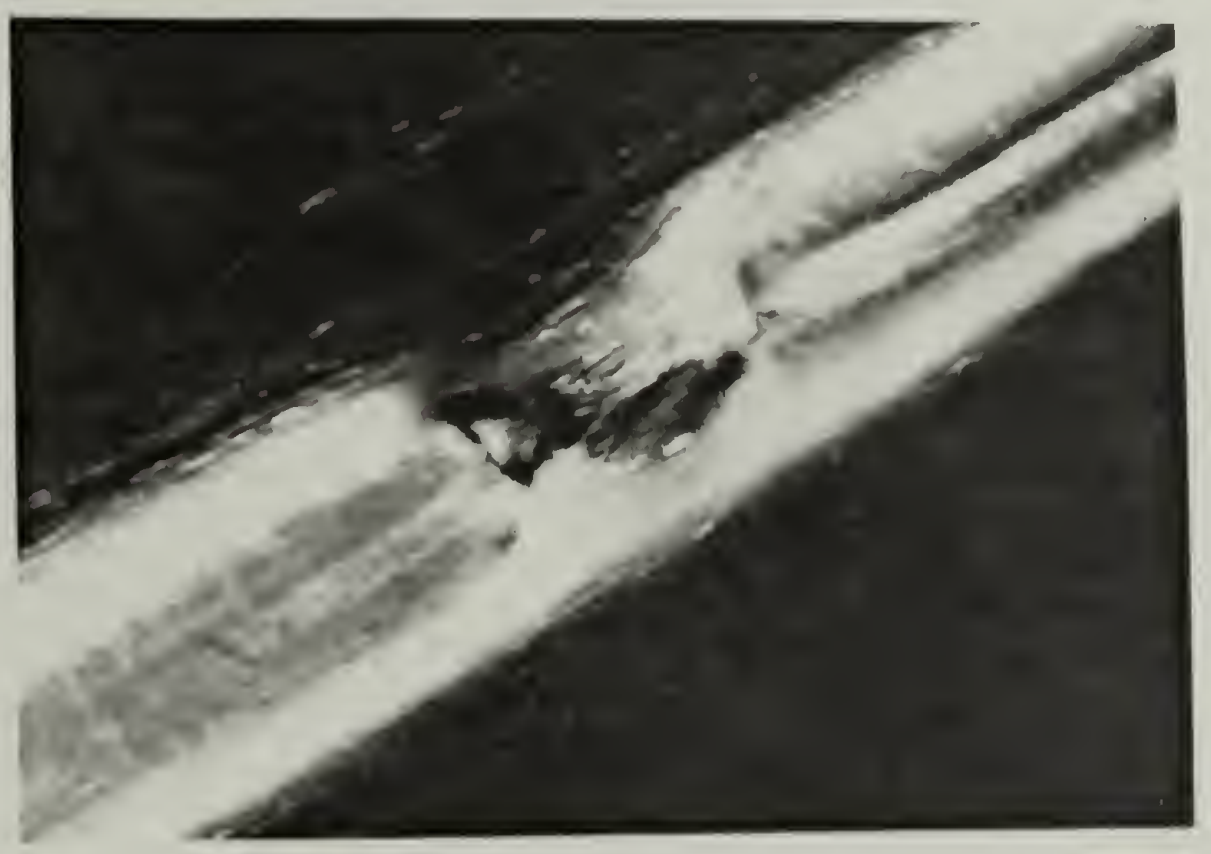


Figure 4.13. Post-treated 20 % Triad2 (2:6:7)/PC fiber that has been solvent etched and observed using cross polarized optical microscopy with a magnification of 200 times. The Micrograph shows highly birefringent Triad2 (2:6:7) fibrils fractured after drawing the fiber at 85°C.

Attempts to distinguish the Triad2 phase within the post-drawn PET fibers were not successful. Due to the high degree of PET crystallinity and the chemical similarity of the two blend components a satisfactory sample preparation technique could not be found. However in order to dramatically improve upon the 17 GPa modulus of neat PET the Triad2 phase would need have a significantly greater modulus than was apparent in either

the PET or PC as-spun systems. Furthermore, if it is assumed that drawing of the PET blends breaks up the Triad2 phase as found in the PC systems, it is unlikely that mechanical reinforcement is responsible for any obtained modulus improvements. Since the PET blends were drawn approximately double that of the PC systems, damage to the Triad2 phase should be even more severe. This further indicates that a matrix modification phenomena is probably responsible for the observed modulus enhancements rather than any inherent properties of the Triad2 block copolymer.

4.5 Conclusions

The degree of mechanical enhancement obtained in the fibers incorporating 20 wt. % of the Triad2 (2:6:7) block copolymer depended upon the chosen matrix material and the processing conditions. The PET matrix systems did not exhibit any modulus improvements until after post-treatment of the fibers. Following post-treatment the blends exhibited a modulus of 24 GPa, an increase of 40 % compared to the PET control fiber. The free shrinkage of the blended PET fiber was also reduced from 10 to 8 percent after post-treatment. Thus the dimensional stability of the fiber was improved along with the mechanical performance.

The PC systems exhibited a 1 GPa modulus increase in the as-spun fiber blends, but improvement was negligible after fiber post-treatment. Application of the simple rule of mixtures estimated that the neat Triad2 block copolymer had a modulus of only 9 GPa. The PC blends also indicated that the dimensional stability of the neat Triad2 polymer was poor. Incorporating 20 wt. percent of Triad2 into the PC matrix essentially doubled the amount of free shrinkage experienced by the fiber at 130°C compared to the PC control.

The morphologies of the as-spun and post-treated fibers suggest that different mechanisms of reinforcement are occurring depending upon the matrix material selected. The as-spun PET fiber blends exhibit some fibril formation but their low aspect ratios and

scarce numbers indicate true mechanical reinforcement is unlikely. The small amount of Triad2 phase observed in the fibers also suggests that some interaction between the blend components may have occurred.

The morphology of the as-spun PC blends was ideal for mechanical reinforcement. The Triad2 phase was elongated into fibrils having essentially infinite aspect ratios within the PC matrix. The large number of high aspect ratio fibrils oriented along the fiber axis combined with the absence of significant modulus improvement is further evidence that Triad2 is not a high performance polymer.

The morphology of the post-treated PC blend indicated that fiber drawing reduces the ability of the Triad2 block copolymer to mechanically reinforce either PC or PET. The post-treatment process periodically fractures the Triad2 fibrils within the matrix material effectively reducing their aspect ratio. Thus the modulus enhancement observed in the PET blends is most likely due to a modification of the PET matrix.

Thermal results indicate that the Triad2 block copolymer is capable of modifying the PET matrix phase. DSC results show a 5°C shift in the Tg of PET when blended with Triad2, suggesting some interaction between components is likely. The addition of Triad2 to PET also dramatically affects the crystallization behavior of PET. The incorporation of Triad2 increases the degree PET crystallinity and decreases the cold crystallization temperature. Thus the Triad2 performs as an effective nucleating agent for PET. If the nucleating effect also occurs during the drawing process, the enhanced mechanical performance of the PET blends could be attributed to an increase in fiber crystallinity.

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CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1 Summary of the Results and Conclusions

Several novel blend systems containing semi-rigid thermotropic liquid crystalline polymers and poly(ethylene terephthalate) have been investigated. The work focused primarily on the ability of the TLCP's to improve the performance of PET fibers. To determine if a system exhibited desirable characteristics, a screening procedure was developed to assess the various blends quickly and efficiently. Limited amounts of liquid crystalline polymer, typically 6 to 9 grams, required evaluations to focus on compositions ranging from 2 to 20 wt.- % LCP. Fibers were obtained by melt extrusion and the effect of processing conditions, i.e. spinning temperature, stretch ratio, and post treatment evaluated. Residence times in the extruder were kept to a minimum to prevent transesterification and degradation. The fibers were tested for mechanical performance, dimensional instability (shrinkage), and the development of shrinkage stresses. Test results were used to determine the critical parameters necessary for in-situ reinforcement and to develop strategies for improving LCP architecture and processing techniques.

The PME-b-PET and PME-b-PBT block copolymers did not significantly reinforce the PET fibers, but minor improvements in fiber modulus were apparent in both systems. The blends could also be processed and post-treated at the 20 % loading level, indicating some compatibility was attained. The fact that only moderate modulus improvements were observed may have been due to the incorporation of 50 wt. % flexible moieties into

the main chain. This may have reduced the moduli of the block copolymers to such an extent that significant reinforcement was not possible at low loading levels.

The incorporation of either PET or PBT flexible moieties into the block copolymer did not affect the reinforcement characteristics. The tensile properties of the two block copolymer systems were essentially identical. This is significant because the PME-b-PBT copolymer had higher molecular weight, better processability, and greater thermal stability.

Although the PBEM material should be stiffer than the block copolymers, significant modulus improvement was not observed. Furthermore as the weight percent LCP was increased from 5 to 20 % a dramatic skin-core morphology developed indicating incompatibility between the blend components. However, steady shear viscometry showed that PBEM has the potential to be an excellent processing aid for PET. At 270° C, concentrations as low as 2.5 wt.% PBEM exhibited a 75% reduction in viscosity. This could permit processing at lower temperatures reducing the threat of degradation. The spinning of higher molecular weight PET may also be possible; use of higher molecular weight PET in fiber spinning could dramatically increase the tenacity of the fibers.

The random copolymer system was found to have improved the mechanical properties compared to neat PET fibers. Fibers containing only 5 % TLCP exhibited a 50 % increase in modulus, while maintaining an ultimate strength equivalent to the PET control. The mechanism of reinforcement is unclear but DSC evidence suggests that the LCP is modifying the PET matrix. The Tg's of the blend systems were essentially identical to the PET control indicating that either the Random Copolymers has a similar glass transition temperature or that little no interaction has occurred between the two materials. The Random Copolymer did appear to be an efficient nucleating agent for PET. The rate and the extent of PET crystallization both increased with the addition of the LCP material.

Scanning Electron Microscopy observations of fractured fiber cross sections revealed that the TLCP phase was elongated into fibrils. The fibrils were 0.2 to 0.4 μm in diameter and uniformly dispersed throughout the PET matrix. The spinning temperature and draw ratio were critical processing parameters that dramatically affected mechanical properties and thermal behavior. Processing below the LC→LC transition of the Random Copolymer resulted in only minor modulus improvements. Processing with die temperatures of approximately 310°C resulted in a decrease in fiber tenacity and the lowest modulus of all the Random Copolymer blend systems. As the draw ratio of the 5% blend fiber, spun at 290°C, was increased the modulus and ultimate strength improved. The thermal behavior of the 5 % system, as determined by free shrinkage and force-temperature experiments, was similar to the PET control.

Several different Triad-b-PBT block copolymer systems were investigated to determine the optimum molecular architecture necessary for PET reinforcement. Variables that were considered included: block size, mesogen content, PBT content, and mesogen rigidity.

The quantity of PBT incorporated into the Triad4 copolymers dramatically affected the thermal behavior or these systems but had little influence on the ability of the LCP to reinforce PET. Reducing the size of the PBT flexible block from twenty-one to three units increased the temperature of the primary melting transition (T_m1) by 17°C and decreased the degradation temperature, as determined by TGA, by 24°C. The length of the PBT block also influenced the amount of free shrinkage experience by the blend fibers. The greater the size of the PBT blocks the more free shrinkage demonstrated by the blends. Fibers containing 20 % Triad4 (2:4:21) exhibited 14 % free shrinkage whereas fibers incorporating 20 % Triad4 (2:4:3) only shrank 10 %. The length of the mesogenic block in the copolymer also had a profound impact on blend thermal behavior. Increasing the

mesogen block length from four to six units increased the degradation temperature of the copolymer by 34°C. A 20 % blend of Triad4 (2:6:7) also exhibited greater thermal stability than observed in the Triad4 (2:4:7) systems.

As stated earlier the amount of PBT incorporated into the Triad4 copolymers did not appear to significantly influence the tensile performance of the blends. The mechanical performance of the blends containing Triad4 were essentially independent of PBT content regardless of the wt. % Triad4 copolymer incorporated into the blends i.e. the 5, 10, and 20 wt. % Triad4 systems had very similar tensile performance. Reinforcement of the PET fiber was not observed until the mesogen block was increased from four to six units. The 20 % blend of Triad4 (2:6:7) exhibited the best tensile properties of the Triad4 systems. The blend had a modulus of 21 GPa compared to 17 GPa for the PET control.

Increasing the stiffness of the mesogenic block resulted in the best mechanical and thermal performance. The 20 % Triad2 (2:4:7) blend had a modulus of 23 GPa and the 20% Triad2 (2:6:7) system had a modulus of 24 GPa. The strength of the 20 % Triad2 (2:4:7) system was also higher than the PET control i.e. 1300 MPa versus 1100 MPa. The addition of 20% Triad2 (2:6:7) to PET also reduced the free shrinkage of the fibers. Comparing fiber samples having a maximum shrinkage stress of approximately 80 MPa, the blended fiber exhibited 7 % free shrinkage while the PET control had 9 %. This is approximately a 30 % increase in fiber thermal stability at 190C. The Triad2 (2:6:7) also exhibited superior free shrinkage characteristics when compared to the 20 % Triad4 (2:6:7) system which had 8% free shrinkage. Thus the more rigid Triad2 mesogen appears to be more efficient at reducing dimensional instabilities and increasing the mechanical performance of PET fiber. The spinning temperature and draw ratio were found to be critical processing parameters that dramatically affected mechanical properties and thermal behavior. Processing the 20 % Triad2 (2:4:7) blend at 290C caused

significant degradation whereas processing at 280C resulted in improved mechanical performance. As the draw ratio of the 20% Triad2 (2:6:7) fiber, spun 280°C, was increased the modulus and ultimate strength improved.

Scanning Electron Microscopy observations of fractured fiber cross sections revealed that the Triad2 (2:6:7) phase was evenly distributed throughout the fiber cross-section with the exception of a 1 μm skin region rich in LCP content. The size of the LCP phase varied depending upon the location within the fiber. Interior particles ranged from 0.5 to 2 μm in diameter while the particles located in the skin region appeared to have diameters in the range of 0.05 to 0.2 μm. The shape of the LCP phase also varied and appeared to consist of both particulate and elongated geometry's. The fibrils were 1 to 2 μm in diameter.

The degree of mechanical enhancement obtained in the fibers incorporating 20 wt. % of the Triad2 (2:6:7) block copolymer depended upon the chosen matrix material and the processing conditions. The PET matrix systems did not exhibit any modulus improvements until after post-treatment of the fibers. Following post-treatment the blends exhibited a modulus of 24 GPa, an increase of 40 % compared to the PET control fiber. The free shrinkage of the blended PET fiber was also reduced from 10 to 8 percent after post-treatment. Thus the dimensional stability of the fiber was improved along with the mechanical performance.

The PC systems exhibited a 1 GPa modulus increase in the as-spun fiber blends, but improvement was negligible after fiber post-treatment. Application of the simple rule of mixtures estimated that the neat Triad2 block copolymer had a modulus of only 9 GPa. The PC blends also indicated that the dimensional stability of the neat Triad2 polymer was poor. Incorporating 20 wt. percent of Triad2 into the PC matrix essentially doubled the amount of free shrinkage experienced by the fiber at 130°C compared to the PC control.

The morphologies of the as-spun and post-treated fibers suggest that different mechanisms of reinforcement are occurring depending upon the matrix material selected. The as-spun PET fiber blends exhibit some fibril formation but their low concentration and small aspect ratios indicate true mechanical reinforcement is unlikely. The small amount of Triad2 phase observed in the fibers also suggests that some interaction between the blend components may have occurred.

The morphology of the as-spun PC blends was ideal for mechanical reinforcement. The Triad2 phase was elongated into fibrils having essentially infinite aspect ratios (i.e. > 10,000) within the PC matrix. The large number of high aspect ratio fibrils oriented along the fiber axis combined with the absence of significant modulus improvement is further evidence that Triad2 is not a high performance polymer.

The morphology of the post-treated PC blend indicated that fiber drawing reduces the ability of the Triad2 block copolymer to mechanically reinforce either PC or PET. The post-treatment process periodically fractures the Triad2 fibrils within the matrix material effectively reducing their aspect ratio. Thus the modulus enhancement observed in the PET blends is most likely due to a modification of the PET matrix.

Thermal results indicate that the Triad2 block copolymer is capable of modifying the PET matrix phase. DSC results show a 5°C shift in the Tg of PET when blended with Triad2, suggesting some interaction between components is likely. The addition of Triad2 to PET also dramatically affects the crystallization behavior of PET. The incorporation of Triad2 increases the degree PET crystallinity and decreases the cold crystallization temperature. Thus the Triad2 performs as an effective nucleating agent for PET. If the nucleating effect also occurs during the drawing process, the enhanced mechanical performance of the PET blends could be attributed to an increase in fiber crystallinity.

5.2 Suggestions for Future Work

Although the results of this work suggest that the semi-rigid rods do not perform as true mechanical reinforcing agents, the improvements in mechanical and thermal performance of PET fibers are respectable. Furthermore, the blends based on Triad TLCP's have provided valuable insight for the formulation of a second generation of novel TLCP's. For instance, the length and stiffness of the mesogenic unit essentially determine the effectiveness of the TLCP as a reinforcement agent, whereas the length of the flexible PBT unit can influence the dimensional instability of the blends.. The weight percent TLCP incorporated into the fibers can also determine the processability of the systems and the extent of property improvement.

Based upon these trends, it is proposed to investigate a Triad2 (2:8:7) or a Triad2 (2:12:7) block copolymer system. These polymers have a higher rod content than the 2:4:7 system that achieved a modulus of 24 GPa and would determine if an upper limit has been attained or if greater improvements are possible. It is also proposed to alter the size of the random coil segment in the Triad 4 materials. A smaller flexible group such as an ethylene unit may enhance the performance of these systems and potentially reduce the amount of LCP necessary for reinforcement below the 20% currently used. Finally it is proposed to evaluate main chain flexible systems that have been synthesized without a diad sequence in the polymer chain. Although a minor change structurally, the elimination of the diad sequence may have a profound impact on the thermal behavior of the triad polymers and thus affect the processing and mechanical performance of these systems.

A random TLCP copolymer based on monoethoxy hydroquinone, terephthaloyl chloride, and ethylene glycol has been found to provide the best mechanical performance to date. Fibers containing only 5% TLCP exhibited a 50% increase in modulus, while

maintaining an ultimate strength equivalent to neat PET fibers. Attempts to blend alternating block copolymers based on the same mesogenic moiety did not result in PET reinforcement; however, the rod content in these systems may have been too low.

It is proposed to increase the mesogen content of the alternating monoethoxy based block copolymers to determine if the results can be reproduced using a controlled LCP architecture. As the copolymers become stiffer, improvements similar to those observed with the random copolymer would be expected. Modification of the random copolymer system should also be attempted. The effect of molecular weight on blend performance and processability should be investigated. If high molecular weight materials are not necessary due to the unique reinforcement mechanism, lower molecular weight samples may be desirable for viscosity reduction during processing. A reduction in melt viscosity would save energy or potentially allow higher molecular weight PET material to be processed. Higher PET molecular weights could improve fiber tenacity.

A detailed morphological investigation of the blends exhibiting good mechanical performance is also suggested. The results of this investigation indicate that the LCP's are affecting either the crystallization behavior of the PET matrix or increasing the number of tie chains between crystallites in some manner. A thorough investigation using WAXD and DSC techniques should be able to characterize the crystal structure and the extent of crystallinity within the fiber. DSC experiments could be performed on the preprocessed powders and the post-treated fibers to quantitatively determine the influence of the LCP on the rate and extent of PET crystallization. Birefringence experiments would also provide useful information on the orientation of the amorphous material within the fiber, however, decoupling the LCP and PET contributions may be challenging.

Finally, optimization of processing and fiber post-treatment should be attempted. This would permit a more complete and systematic study of promising TLCP materials

since better control of the fiber forming process could be maintained. Possible modifications include: adding a pressure transducer to the Randcastle Extruder so that measures of viscosity during spinning could be obtained and modification of the cold and hot drawing post-treatment process such that tension, fiber diameter and draw ratio can be continuously monitored.

APPENDIX

TYPICAL STRESS-STRAIN CURVES

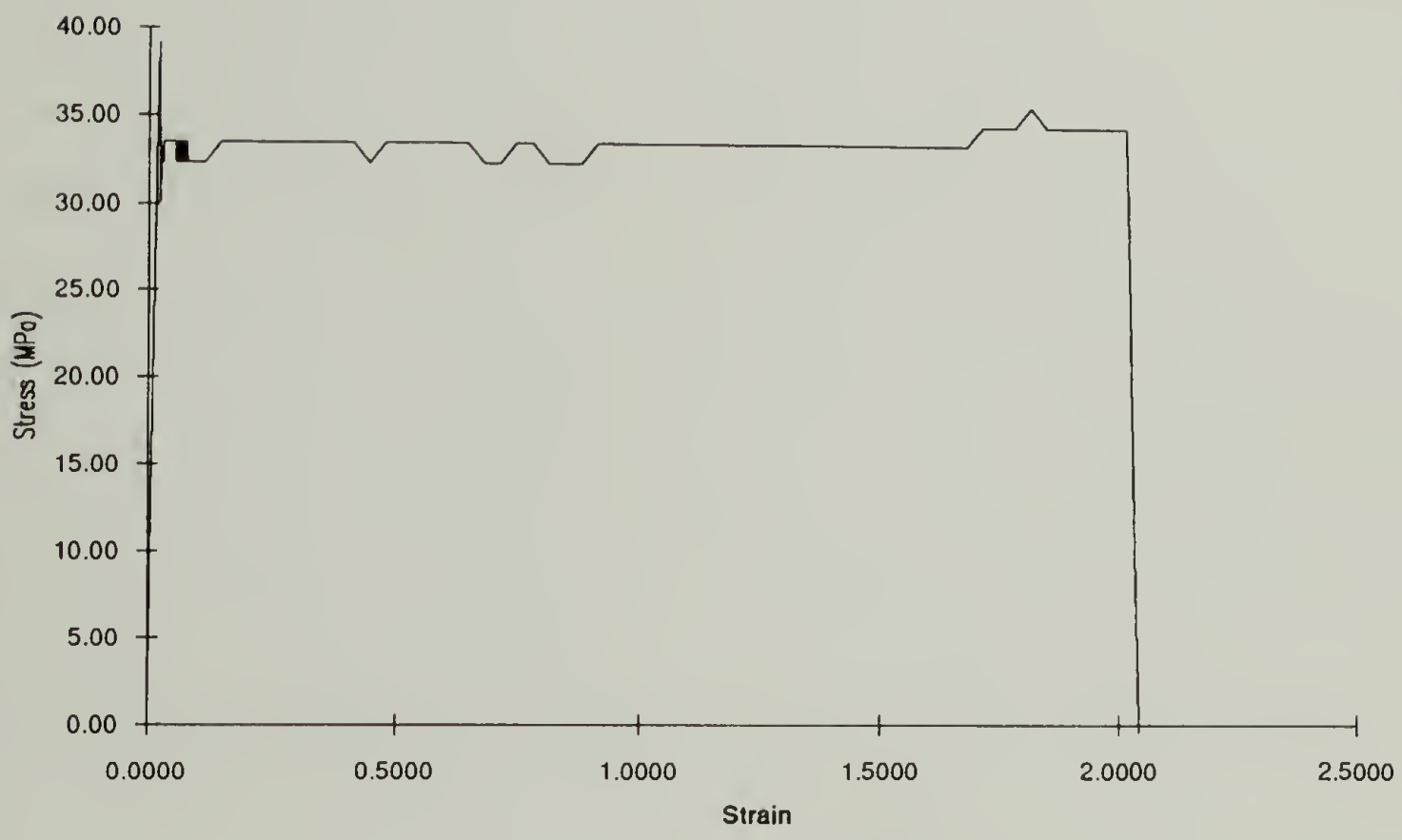

Figure A-1. Stress-strain curve for as-spun neat PET with a diameter of 86 μm and a stretch ratio of 335.

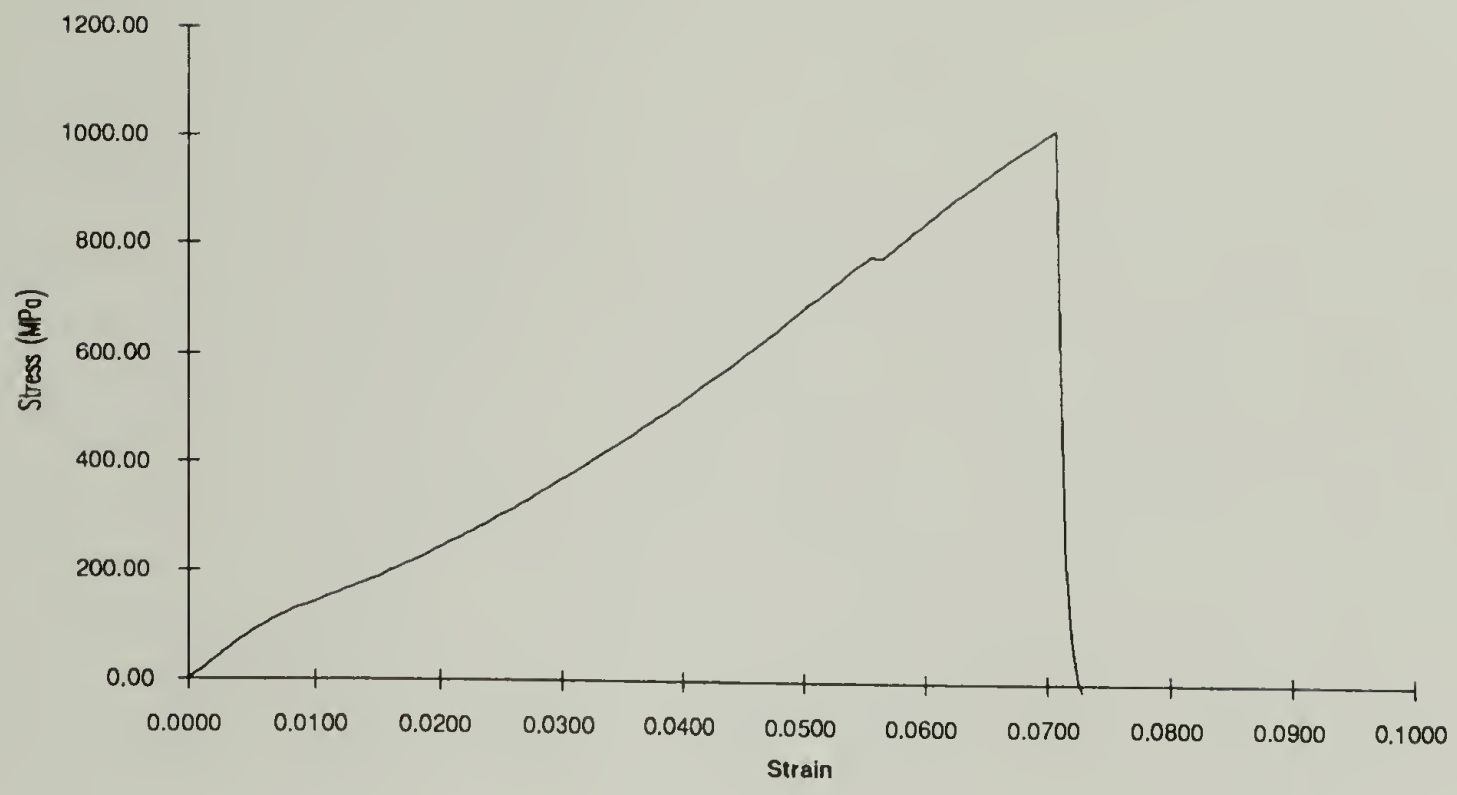

Figure A-2. Stress-strain curve for neat PET with a diameter of 38 μm and a final draw ratio of 5.1.

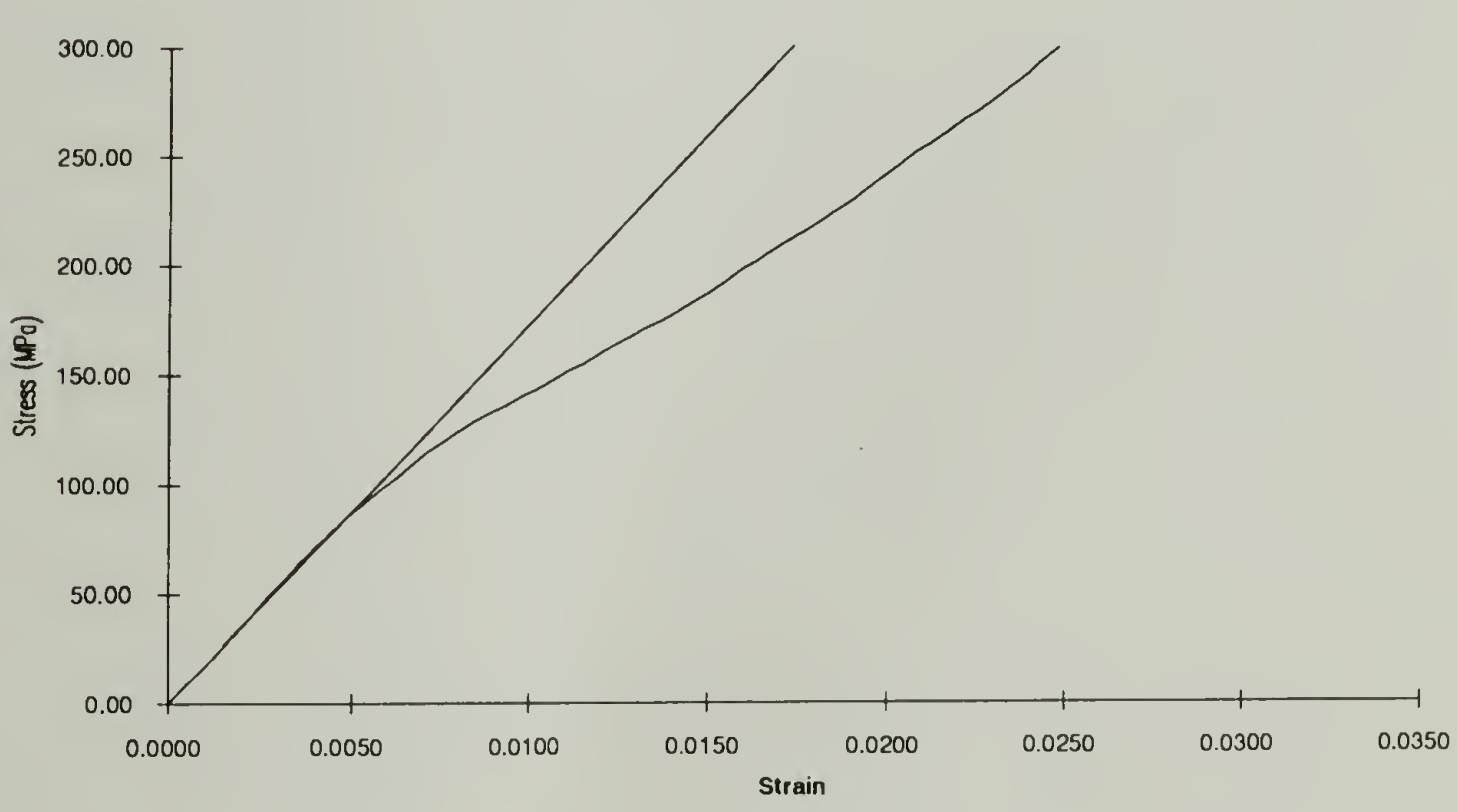

Figure A-3. Young's modulus determination from the best linear fit through the initial region of the stress-strain curve for neat PET with a diameter of 38 μm and a final draw ratio of 5.1.

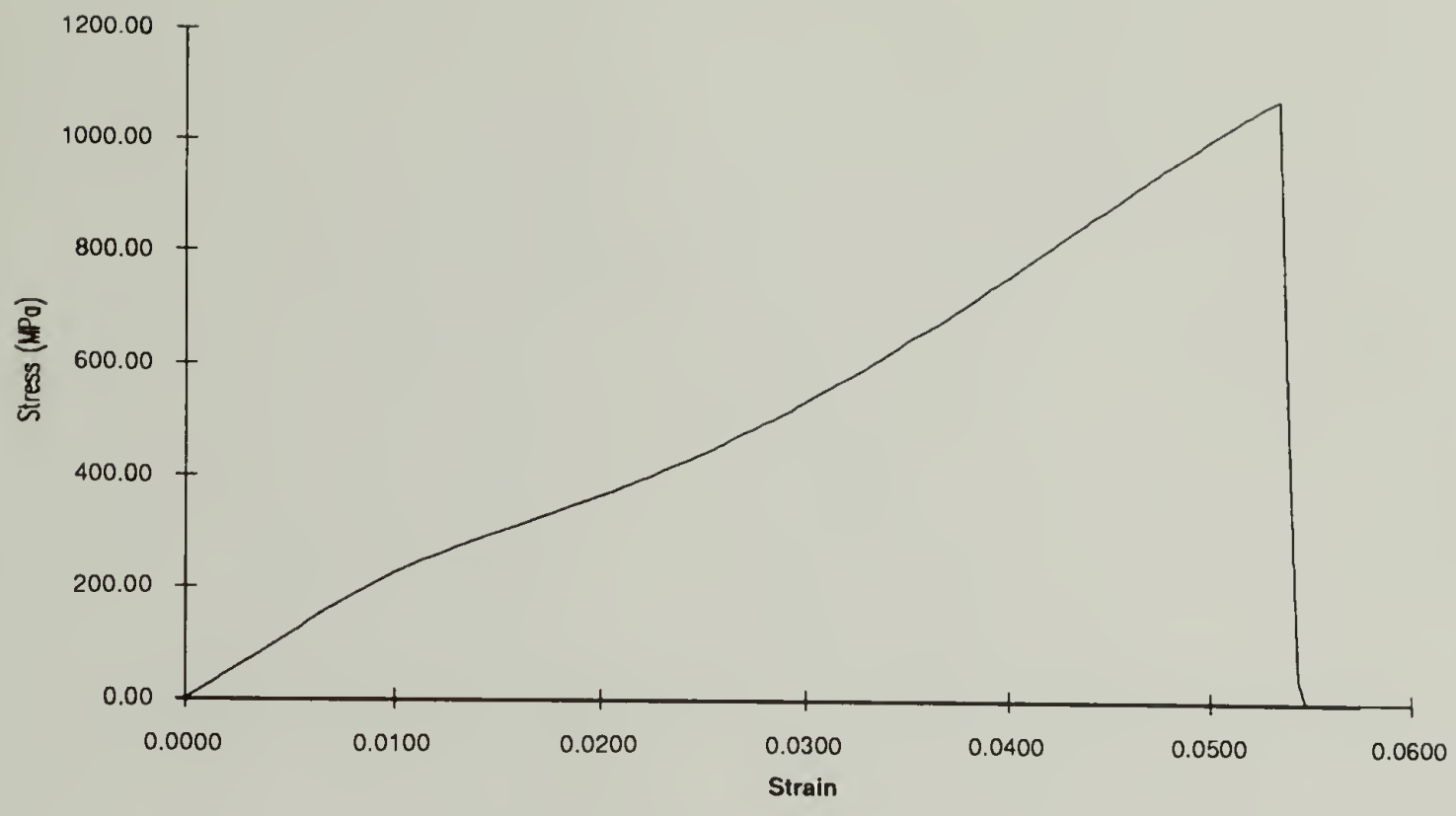

Figure A-4. Stress-strain curve for a 5 % Random Copolymer blend with a diameter of 32 μm and a final draw ratio of 5.5.

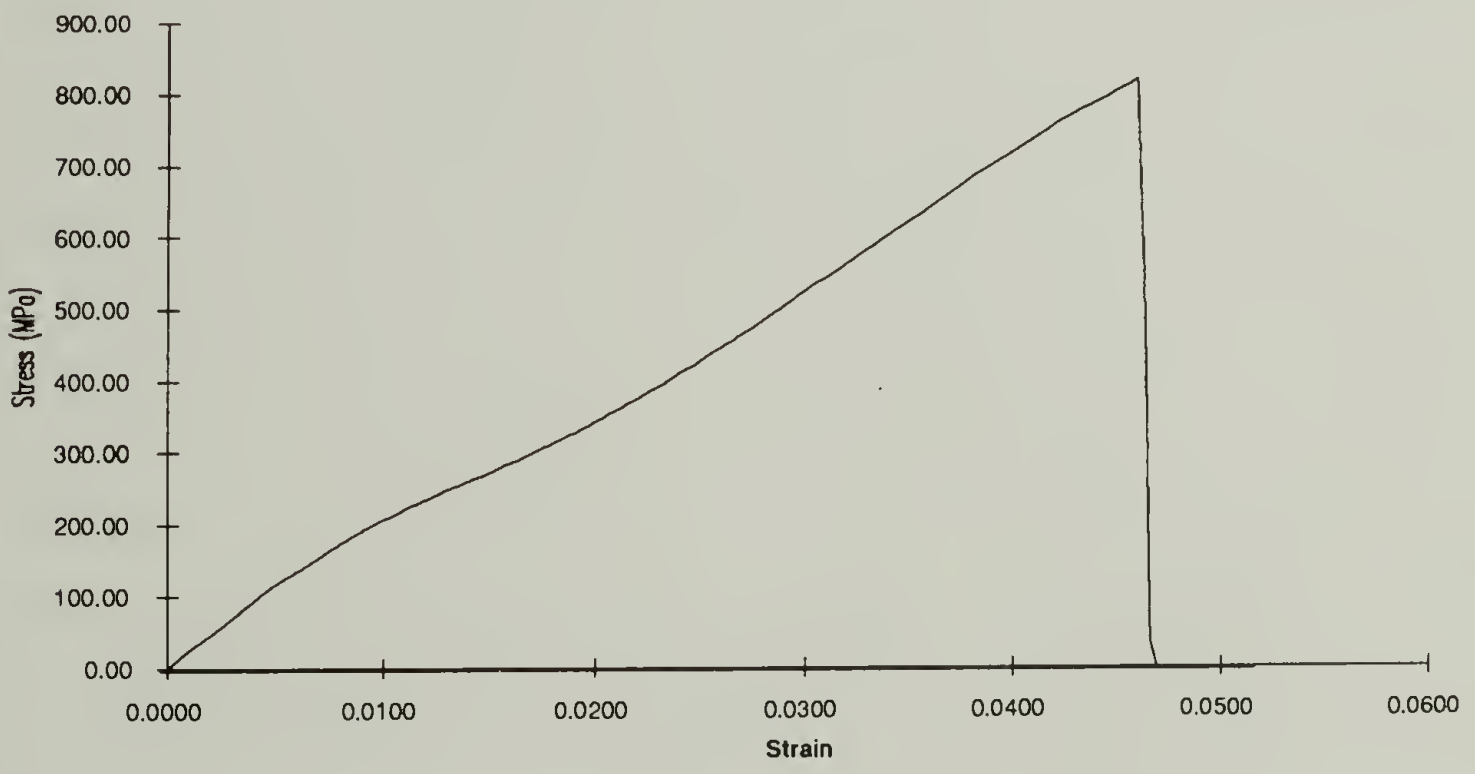

Figure A-5. Stress-strain curve for a 20 % Triad2 (2:6:7) blend fiber with a diameter of 36 μm and a final draw ratio of 5.5.

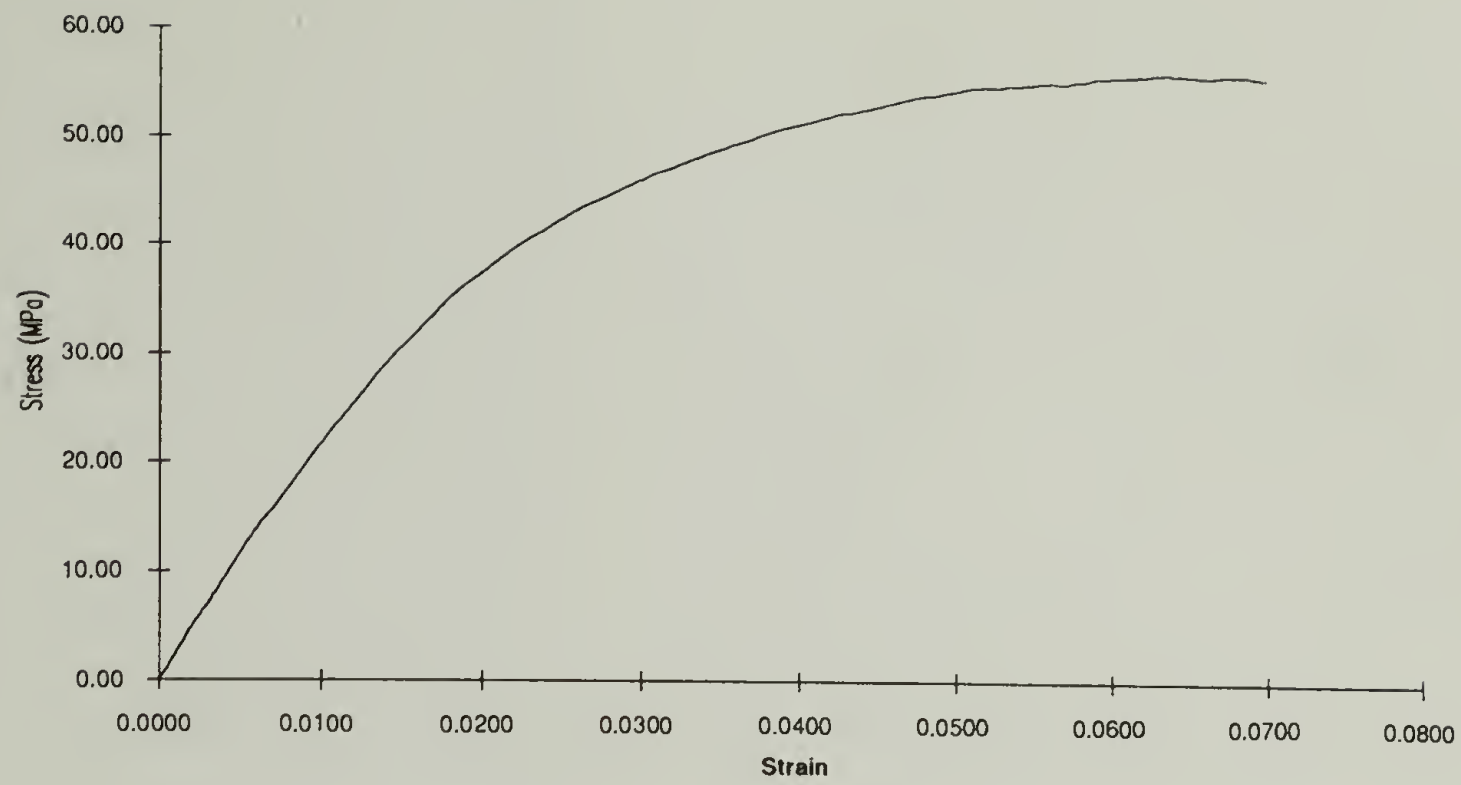

Figure A-6. Stress-strain curve for as-spun neat PC with a diameter of 75 μm and a stretch ratio of 441. The test was stopped after 7 % strain.

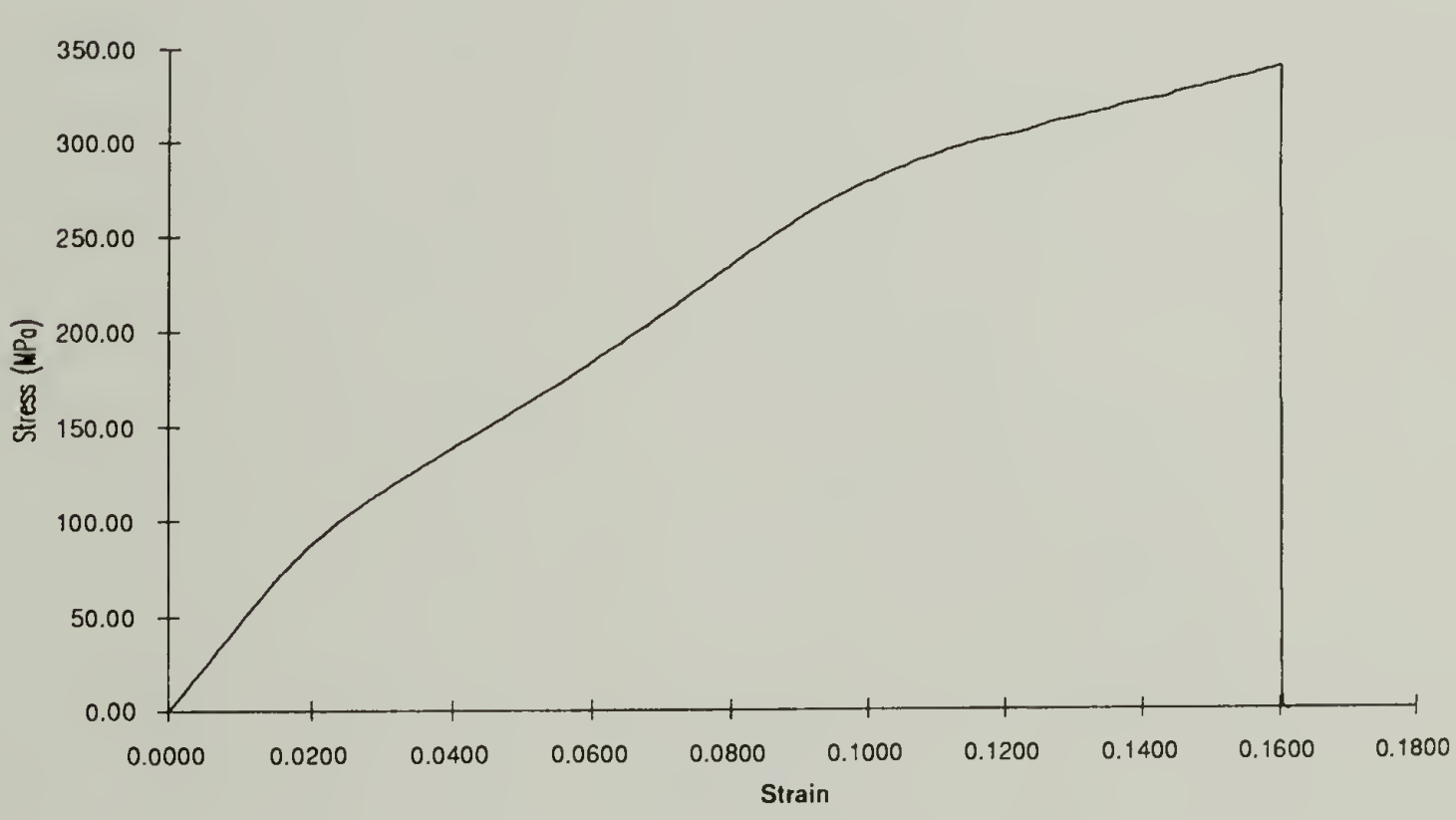

Figure A-7. Stress-strain curve for cold drawn neat PC with a diameter of 58 μm and a final draw ratio of 1.7.

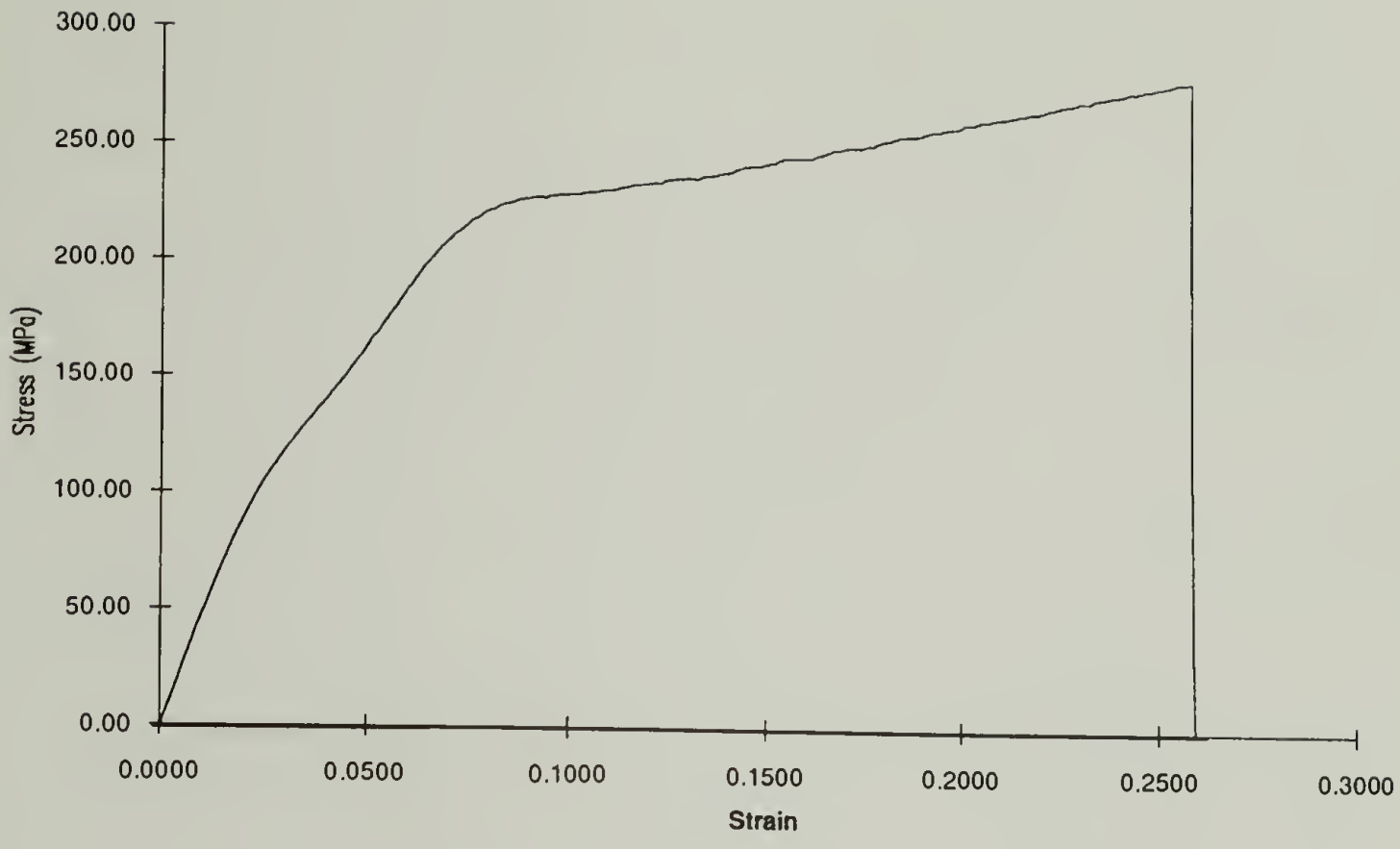

Figure A-8. Stress-strain curve for a 20 % Triad2/PC fiber blend with a diameter of 57 μm and a final draw ratio of 2.1.

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